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***Ab Initio* Calculation of the excited states
of some diatomic molecular ions**

by

Gap-Sue Kim

**This thesis is submitted in fulfilment of the requirements of the degree
of doctor of philosophy of the University of Warwick.**

1997

DECLARATION

**The work described here has not been submitted previously in respect
of any degree or qualification.**

To mum and dad

,

During the course of this work we have published three papers as follows:

1) An *ab initio* study of the excited states of the molecular ions NF^+ and PCl^+

By GAP-SUE KIM and DAVID M. HIRST

Molecular Physics, 1995, Vol. 86, No. 5, 1183-1193

2) A theoretical study of the excited electronic states of the molecular ion BBr^+

By GAP-SUE KIM and DAVID M. HIRST

Molecular Physics, 1997, Vol. 90, No. 1, 43-47

3) Ab initio potential-energy curves for excited electronic states of the molecular ion AsCl^+

Gap-Sue Kim, David M. Hirst

Chemical Physics Letters 264 (1997) 134-138

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ABSTRACT

This thesis aims to provide theoretical information by using *ab initio* calculations as a bridge between theory and experiment. This thesis presents calculations of potential energy curves for the diatomic molecular ions NF^+ , PCl^+ , AsCl^+ and BBr^+ and preliminary potential energy surfaces for $\text{HC} + \text{NO}$.

For the diatomic molecular ions, this work presents the low-lying electronic states of NF^+ , PCl^+ , AsCl^+ and BBr^+ correlating with the lowest dissociation asymptotes, namely $\text{N}^+(^3\text{P}) + \text{F}(^2\text{P})$, $\text{P}^+(^3\text{P}) + \text{Cl}(^2\text{P})$, $\text{As}^+(^3\text{P}) + \text{Cl}(^2\text{P})$, $\text{B}^+(^1\text{S}) + \text{Br}(^2\text{P})$ and $\text{B}(^2\text{P}) + \text{Br}^+(^3\text{P})$. In this work CASSCF and CI calculations have been performed with the correlation-consistent valence quadruple-zeta (VQZ) basis sets for NF^+ and PCl^+ , averaged atomic natural orbital (ANO) basis sets for AsCl^+ and BBr^+ , and the correlation-consistent valence double-zeta (VDZ) basis sets for $\text{HC} + \text{NO}$. From the calculations of potential energy curves four bound states, namely $\text{X}^2\Pi$, $\text{A}^2\Pi$, $1^4\Sigma^-$ and $1^4\Pi$, are found for NF^+ , PCl^+ and AsCl^+ , and there are many more bound states, namely $1^2\Sigma^+$, $1^2\Pi$, $2^2\Pi$, $2^2\Sigma^+$, $1^2\Delta$, $1^2\Sigma^-$, $^4\Sigma^+$, $^4\Delta$, and $1^4\Sigma^-$, for BBr^+ . For all the bound states spectroscopic constants have been calculated. For NF^+ , PCl^+ and AsCl^+ our results are in good agreement with the available spectroscopic data. However, for BBr^+ the theoretical values are in disagreement with experimental data. It is suggested that a reinvestigation of the experimental spectrum of this species would be worthwhile. Calculations of transition moments for bound-bound transitions have been carried out.

For $\text{HC} + \text{NO}$ the linear structures for $^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$ and $^3\Sigma^-$ states and the bent structure for $^1\text{A}'$ state have been calculated. These calculations were intended to obtain potential energy surfaces for the reaction of HC with NO . However, due to the lack of time left, only preliminary calculations are completed. Reaction without an activation barrier may occur for a non-collinear approach of HC to NO .

Abbreviations

ANO	Averaged atomic natural orbital basis set
CASSCF	Complete active-space self-consistent field method
CI	Configuration interaction
CISD	Single and double excitations
CSF	Configuration state function
DZ	Double-zeta basis set
DZP	Double-zeta plus polarization basis set
ECP	Effective core potentials
GTO	Gaussian-type orbital
LCAO	Linear combination of atomic orbitals
MC-SCF	Multi-configuration self-consistent field method
MP2	Second-order Møller-Plesset perturbation theory
MRCI	Multi-reference configuration interaction
RHF	Restricted Hartree-Fock method
SCF	Self-consistent field method
STO	Slater-type (exponential) orbital
STO-NG	Expansion of a Slater-type orbital in terms of N Gaussian functions
UHF	Unrestricted Hartree-Fock method
VDZ	Valence double-zeta basis sets
VTZ	Valence triple-zeta basis sets
VQZ	Valence quadruple-zeta basis sets

1. Introduction

Nowadays, with the help of quantum methods accurate theoretical data for diatomic and small polyatomic molecules can be obtained which is of comparable accuracy to experimental data from sophisticated spectroscopic techniques and can provide much useful information about the molecular energy levels. Thus, quantum chemistry makes calculated potential energy surface have an important relationship with experiment and enables theoretical calculations to compare with and predict experimental data.

Chemistry is about chemical reactions, chemical bonding and reaction dynamics.

The potential energy surface helps us to understand those topics mentioned above.

Particularly, the potential energy surface for a diatomic molecule is expressed as a function of the internuclear distance and is usually called the potential energy curve.

The interpretation of potential energy surfaces gives very important information regarding reaction dynamics, electronic configurations, spectroscopic constants and molecular structure.

There are two sorts of chemical problems to make us curious and interested in using a theoretical treatment.

First, very recently interest has increased in the spectroscopic and kinetic properties of oxygen-like molecules such as NF[46,57], NCl[47,48,57,70], PF[52-55], SO[58-63,65] and S₂[62,66] in the ground(³Σ⁻) and low-lying excited states(a¹Δ, b¹Σ⁺) because of potential use as electronic energy storage reservoirs or lasing species in a chemical laser system[12,46]. Also, those oxygen-like molecules have a very important relationship with the chemistry of both the upper atmosphere and interstellar

space because of the relatively high abundances of the component elements. Furthermore, relatively little information has been obtained on the cations of oxygen-like molecules even though there have been spectroscopic studies for the neutral molecules[56,58,65-68,70] and recent gas-phase measurements have determined improved spectroscopic constants for the ground electronic states[49-51].

Second, in the past ten years combustion modelling with *ab initio* electronic structure theory and dynamics has been developed with the help of modern supercomputers[71]. Nitrogen chemistry is one of the most important fields in combustion and atmospheric chemistry. The oxides of nitrogen produced by combustion processes are the key to the formation of photochemical smog in the urban atmosphere and nitric acid derived from NO₂ contributes to acid rain. Other species containing fixed nitrogen include NH₃, HCN, N₂O and amine compounds which can be produced as combustion products and are also of great concern. The chemical reactions of nitrogen compounds in combustion reactions have been the subject of extensive and intensive investigation for more than fifty years[72]. Much of our knowledge of the mechanisms and rate parameters for the gas-phase reactions of nitrogen compounds has come from comparison of calculated kinetic data with experimental data. Sensitivity and rate-of production analyses has been studied to determine which elementary reactions are of great interest in the nitrogen conversion mechanisms.

Those two reasons described above motivate us to choose and to carry out the work described in this thesis.

Our work is divided into two parts which are diatomic molecular ions and nitrogen chemistry in combustion as mentioned above.

For diatomic molecular ions, we have considered four species NF^+ , PCl^+ , AsCl^+ and BBr^+ , which will be described in sections 1.1, 1.2, 1.3 and 1.4 in turn.

For combustion reaction, $\text{CH} + \text{NO}$ has been considered and the description for $\text{CH} + \text{NO}$ will be given in the section 1.5.

The theoretical calculations for diatomic molecular ions have two aims.

As described earlier, one is to produce potential energy curves for excited electronic states and to obtain information about electronic configurations.

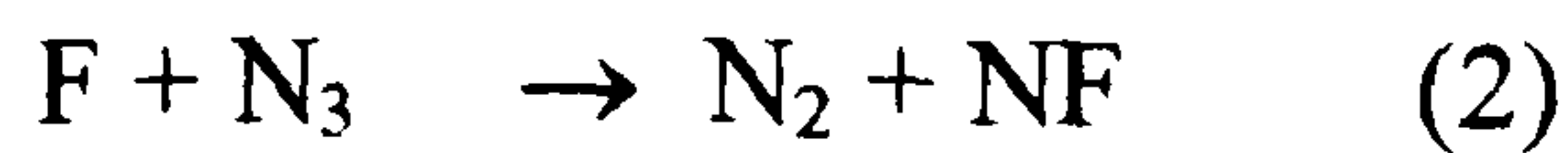
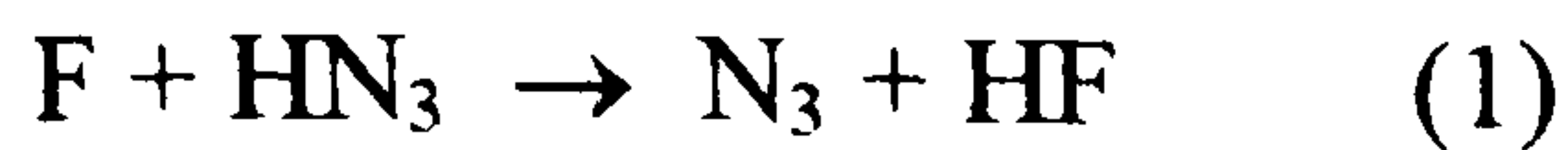
The other is to derive spectroscopic constants for bound states and to compare the theoretical values with the experimental values (where available) and predict constants which have not been determined. Experimental spectroscopy for molecular ions is difficult and theoretical predictions can be of great value. Theoretical estimates can help to reduce long searches.

The aim of the calculations in the area of combustion chemistry is to calculate potential energy surfaces for some important reactions to discover reaction mechanisms, transition states and reaction intermediates and to obtain rate constants using transition state theory

1.1 Introduction for NF^+

NF^+ is one of the Group 5 diatomic monohalide cations with 11 valence electrons. Other ions in this series include NCl^+ [1,7], PCl^+ [8,9] and PF^+ [1,7]. Even though the Group 6 diatomic cations O_2^+ [2,64,68,69], SO^+ [3-5], SeO^+ [6] and S_2^+ [34] have been well investigated, relatively little spectroscopic information is available for the Group 5 diatomic monohalide cations. Both the NF radical and O_2 have the same $^3\Sigma^-$ ground state and low-lying $^1\Delta$ and $^1\Sigma^+$ excited states and also are isoelectronic. Recently interest in the NF free radical has increased due to its potential use in the atomic iodine chemical laser. The identification of an energy-transfer process between $\text{O}_2(^1\Delta_g)$ and $\text{I}(^2\text{P}_{3/2})$ has led to the suggestion that the similar state of NF might be used as the energy source in the chemical pumping process [11,12]. Because of recent interest in the NF radical, investigations have been made to find its first ionization potential and also to identify the observed ionic states with photoelectron spectroscopy and *ab initio* calculations. There have been many values from photoelectron spectroscopy for the first ionization potential of NF before but considerable differences have existed between them. Electron impact mass spectrometric studies for NF_3 provided estimates of the first adiabatic ionization potential for NF ranging from 12.0 ± 0.3 [13] to 13.1 ± 0.2 eV [14]. On the other hand, restricted *ab initio* Hartree-Fock calculations have been performed for both $\text{NF}(X^3\Sigma^-)$ and $\text{NF}^+(X^2\Pi)$ giving an estimate of 13.2 ± 0.3 eV for the first vertical ionization potential [14,15] after approximate allowance is made for the change in correlation energy on ionization. Also, a variety of kinetic and spectroscopic studies has been performed for $\text{NF}(X^3\Sigma^-)$ and

NF($a^1\Delta$)[16-23]. For this work, the NF radical was obtained from the rapid gas-phase reactions[24].



HN₃ was obtained in the gas phase by heating a previously dried mixture of sodium azide and excess stearic acid in a flask. Fluorine atoms were produced from a microwave discharge(2.45 GHz) of molecular fluorine in helium. The NF radical was investigated in a photoelectron spectrometer.

For *ab initio* calculations the ground-state electronic configuration of NF is expressed as $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^2$

Ab initio SCF molecular orbital calculations were carried out for both the $X^3\Sigma^-$ and $a^1\Delta$ neutral states and the ionic states with the ATMOL3 suite of program[25] at the equilibrium bond length of neutral NF($X^3\Sigma^-$) obtained from optical spectroscopy[21].

For ionization of the $X^3\Sigma^-$ state of NF, the ionic states of NF⁺ considered were the states $X^2\Pi$, $^4\Sigma^-$ and $^4\Pi$ arising from the $(2\pi)^{-1}$, $(5\sigma)^{-1}$ and $(1\pi)^{-1}$ ionizations whereas, for ionization of NF($a^1\Delta$), the ionic states were NF⁺ $^2\Delta$ and $^2\Phi$ states. For these *ab initio* calculations a STO double-zeta basis set of Clementi[26] was used with added polarization functions with the exponents N(2.18) and F(2.01).

With the He I photoelectron spectrum from the F + HN₃ reaction two bands with resolved vibrational structure have been observed[7]. For these two bands the vertical ionization potential energies were 11.21 ± 0.01 and 12.63 ± 0.01 eV, corresponding to

the ionization processes $\text{NF}^+(\text{X}^2\Pi) \leftarrow \text{NF}(\text{a}^1\Delta)$ and $\text{NF}^+(\text{X}^2\Pi) \leftarrow \text{NF}(\text{X}^3\Sigma^-)$ respectively. Interpretation of the vibrational structure gave $\omega_e = 1520 \pm 40 \text{ cm}^{-1}$ and $\omega_e x_e = 10 \pm 6 \text{ cm}^{-1}$ for $\text{NF}^+(\text{X}^2\Pi)$. For a range of equilibrium bond lengths a series of calculations has been carried out to obtain the best fit from the observed and calculated vibrational component intensities. The equilibrium bond length of $\text{NF}^+(\text{X}^2\Pi)$ was computed to be 1.178 ± 0.004 and $1.182 \pm 0.004 \text{ \AA}$ from the $\text{NF}(\text{X}^3\Sigma^-)$ and $\text{NF}(\text{a}^1\Delta)$ states respectively. Finally, a value of $r_e = 1.180 \pm 0.006 \text{ \AA}$ was derived for the $\text{X}^2\Pi$ state of NF^+ .

As far as we are aware, no previous optical spectroscopic studies have been reported for any ionic states of NF. Given the limited experimental information available we have carried out the calculation of potential energy curves of NF^+ . An understanding of atomic and diatomic energy levels is required before performing this work.

First of all, atomic states consist of two pairs which are either neutral nitrogen(N) and fluorine cation(F^+) or nitrogen cation(N^+) and neutral fluorine(F).

N and N^+ are the very important atomic components in atmospheric and nitrogen chemistry and are of astrophysical interest. Atomic nitrogen has three low lying states which are ^4S , ^2D and ^2P , with the ground state being the ^4S state. There are three low lying states for the nitrogen cation. The ^3P state is the ground state of the nitrogen cation and the excited states are ^1D and ^1S . The relative energy levels of these two states N and N^+ are given in table 1.1. The energy difference between neutral nitrogen and nitrogen cation (the ionization potential) has the experimental value

117345 cm⁻¹(14.53 eV)[27]. For F, there exists one valence state, namely the ground state ²P. The fluorine cation has three low lying states ³P, ¹D and ¹S. The ground state of the fluorine cation is ³P. The relative energies of F and F⁺ are shown in table 1.2. The experimental value for the ionization potential of F is 17.42 eV[27].

Secondly to form diatomic states of the ion NF⁺ two dissociation asymptotes should be taken into account which are N⁺ + F and N + F⁺. The relative energies for low lying states of N + F⁺ and N⁺ + F are given in table 1.2 and a correlation diagram showing the various dissociation asymptotes for N⁺ + F and N + F⁺ is given in figure 1.

All electronic states shown in a correlation diagram can be derived from the Wigner-Witmer rules[28]. For our work we have only taken into account the lowest dissociation asymptote N⁺(³P) + F(²P) to limit the number of states to a manageable number. The application of the Wigner-Witmer correlation rules provides the following states correlating with the above dissociation asymptote; ²Σ⁺, ²Σ⁻(2), ²Δ, ²Π(2), ⁴Σ⁺, ⁴Σ⁻(2), ⁴Δ, ⁴Π(2). For the states shown above potential energy curves have been calculated from complete active space SCF(CASSCF) and configuration interaction(CI) calculations using three sorts of basis sets which are vdz(valence double-zeta), vtz(valence triple-zeta) and vqz(valence quadruple-zeta) basis sets. As earlier described, little experimental information is available for NF⁺ so this work will be useful of the prediction of spectroscopic parameters.

Table 1.1

Atomic energies for F and F⁺

Neutral state

$F(^2P) - 0\text{ cm}^{-1}(0\text{ eV})$

Cationic state

$F^+(^3P) - 0\text{ cm}^{-1}(0\text{ eV})$

$F^+(^1D) - 20873\text{ cm}^{-1}(2.5883\text{ eV})$

$F^+(^1S) - 44919\text{ cm}^{-1}(5.5700\text{ eV})$

Atomic energies for N and N⁺

Neutral state

$N(^4S) - 0\text{ cm}^{-1}(0\text{ eV})$

$N(^2D) - 19223\text{ cm}^{-1}(2.3837\text{ eV})$

$N(^2P) - 28840\text{ cm}^{-1}(3.5762\text{ eV})$

Cationic state

$N^+(^3P) - 0\text{ cm}^{-1}(0\text{ eV})$

$N^+(^1D) - 15315\text{ cm}^{-1}(1.8991\text{ eV})$

$N^+(^1S) - 32687.1\text{ cm}^{-1}(4.0532\text{ eV})$

Table 1.2

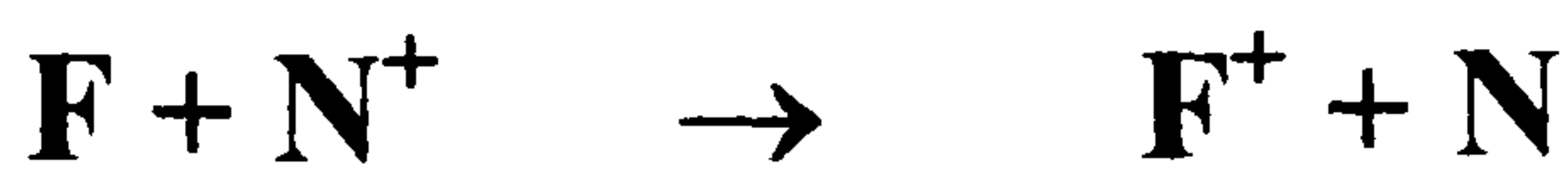
The twelve low-lying states of NF^+ are shown below

Energy values are from Table 1.1

- 1) $\text{N}(^4\text{S}) + \text{F}^+(^3\text{P}) = 0 \text{ cm}^{-1} + 0 \text{ cm}^{-1} = 0 \text{ cm}^{-1} = 0 \text{ eV}$
- 2) $\text{N}(^4\text{S}) + \text{F}^+(^1\text{D}) = 0 \text{ cm}^{-1} + 20873 \text{ cm}^{-1} = 20873 \text{ cm}^{-1} = 2.5883 \text{ eV}$
- 3) $\text{N}(^4\text{S}) + \text{F}^+(^1\text{S}) = 0 \text{ cm}^{-1} + 44919 \text{ cm}^{-1} = 44919 \text{ cm}^{-1} = 5.5700 \text{ eV}$
- 4) $\text{N}(^2\text{D}) + \text{F}^+(^3\text{P}) = 19223 \text{ cm}^{-1} + 0 \text{ cm}^{-1} = 19223 \text{ cm}^{-1} = 2.3837 \text{ eV}$
- 5) $\text{N}(^2\text{D}) + \text{F}^+(^1\text{D}) = 19223 \text{ cm}^{-1} + 20873 \text{ cm}^{-1} = 40096 \text{ cm}^{-1} = 4.9719 \text{ eV}$
- 6) $\text{N}(^2\text{D}) + \text{F}^+(^1\text{S}) = 19223 \text{ cm}^{-1} + 44919 \text{ cm}^{-1} = 64142 \text{ cm}^{-1} = 7.9536 \text{ eV}$
- 7) $\text{N}(^2\text{P}) + \text{F}^+(^3\text{P}) = 28840 \text{ cm}^{-1} + 0 \text{ cm}^{-1} = 28840 \text{ cm}^{-1} = 3.5762 \text{ eV}$
- 8) $\text{N}(^2\text{P}) + \text{F}^+(^1\text{D}) = 28840 \text{ cm}^{-1} + 20873 \text{ cm}^{-1} = 49713 \text{ cm}^{-1} = 6.1644 \text{ eV}$
- 9) $\text{N}(^2\text{P}) + \text{F}^+(^1\text{S}) = 28840 \text{ cm}^{-1} + 44919 \text{ cm}^{-1} = 73759 \text{ cm}^{-1} = 9.1461 \text{ eV}$
- 10) $\text{F}(^2\text{P}) + \text{N}^+(^3\text{P}) = 0 \text{ cm}^{-1} + 0 \text{ cm}^{-1} = 0 \text{ cm}^{-1} = 0 \text{ eV}$
- 11) $\text{F}(^2\text{P}) + \text{N}^+(^1\text{D}) = 0 \text{ cm}^{-1} + 15315 \text{ cm}^{-1} = 15315 \text{ cm}^{-1} = 1.8991 \text{ eV}$
- 12) $\text{F}(^2\text{P}) + \text{N}^+(^1\text{S}) = 0 \text{ cm}^{-1} + 32687.1 \text{ cm}^{-1} = 32687.1 \text{ cm}^{-1} = 4.0532 \text{ eV}$

F(I) I.P(Ionization Potential) = 17.42 eV

N(I) I.P(Ionization Potential) = 14.54 eV



$$\text{I.E(Ionization Energy)} = \text{I.P(F)} - \text{I.P(N)} = 17.42 \text{ eV} - 14.52 \text{ eV} = 2.88 \text{ eV}$$

The dissociation asymptote $\text{F}(^2\text{P}) + \text{N}^+(^3\text{P})$ differs from the dissociation asymptote $\text{F}^+(^3\text{P}) + \text{N}(^4\text{S})$ by **2.88 eV**.

Therefore, if the energy of $\text{F}(^2\text{P}) + \text{N}^+(^3\text{P})$ is regarded as the zero of energy, the energy of $\text{F}^+(^3\text{P}) + \text{N}(^4\text{S})$, (number 1) above, is located **2.88 eV** higher.

Thus, an energy of **2.88 eV** is added to the energy of each dissociation asymptote for **F⁺ + N**(numbers 2 to 9 above).

The relative low-lying energy levels are shown below as follows.

$$10) \text{F}(^2\text{P}) + \text{N}^+(^3\text{P}) = 0 \text{ eV}$$

$$11) \text{F}(^2\text{P}) + \text{N}^+(^1\text{D}) = 1.8991 \text{ eV}$$

$$1) \text{N}(^4\text{S}) + \text{F}^+(^3\text{P}) = 0 \text{ eV} + 2.88 \text{ eV} = 2.88 \text{ eV}$$

$$12) \text{F}(^2\text{P}) + \text{N}^+(^1\text{S}) = 4.0532 \text{ eV}$$

$$4) \text{N}(^2\text{D}) + \text{F}^+(^3\text{P}) = 2.3837 \text{ eV} + 2.88 \text{ eV} = 5.2637 \text{ eV}$$

$$2) \text{N}(^4\text{S}) + \text{F}^+(^1\text{D}) = 2.5883 \text{ eV} + 2.88 \text{ eV} = 5.4683 \text{ eV}$$

$$7) \text{N}(^2\text{P}) + \text{F}^+(^3\text{P}) = 3.5762 \text{ eV} + 2.88 \text{ eV} = 6.4562 \text{ eV}$$

$$5) \text{N}(^2\text{D}) + \text{F}^+(^1\text{D}) = 4.9719 \text{ eV} + 2.88 \text{ eV} = 7.8519 \text{ eV}$$

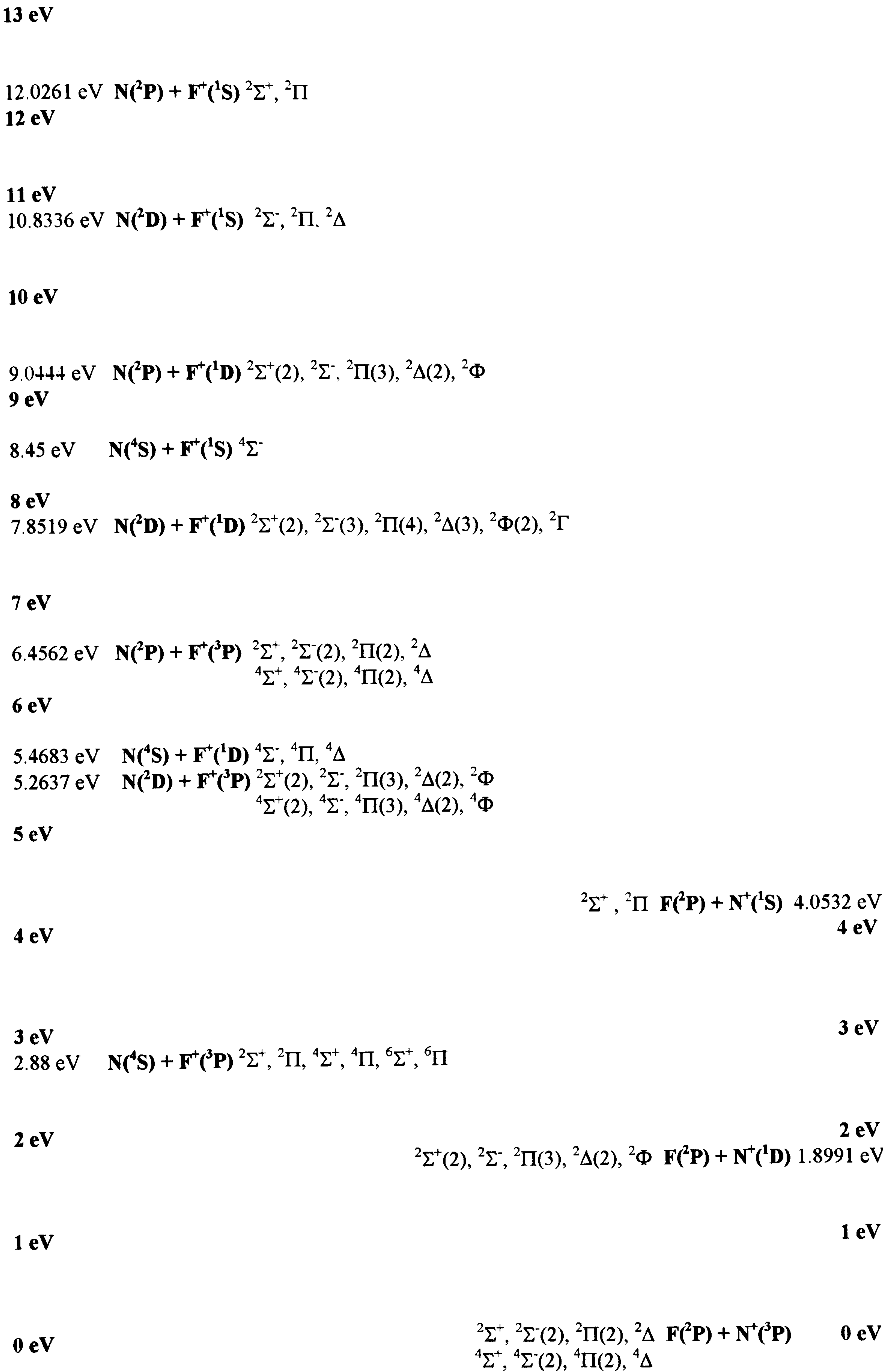
$$3) \text{N}(^4\text{S}) + \text{F}^+(^1\text{S}) = 5.5700 \text{ eV} + 2.88 \text{ eV} = 8.45 \text{ eV}$$

$$8) \text{N}(^2\text{P}) + \text{F}^+(^1\text{D}) = 6.1644 \text{ eV} + 2.88 \text{ eV} = 9.0444 \text{ eV}$$

$$6) \text{N}(^2\text{D}) + \text{F}^+(^1\text{S}) = 7.9536 \text{ eV} + 2.88 \text{ eV} = 10.8336 \text{ eV}$$

$$9) \text{N}(^2\text{P}) + \text{F}^+(^1\text{S}) = 9.1461 \text{ eV} + 2.88 \text{ eV} = 12.0261 \text{ eV}$$

Figure 1. Correlation diagram for the low lying states of NF⁺



1.2 Introduction for PCl^+

PCl^+ is also one of the Group 5 monohalide diatomic cations with 11 valence electrons but there is rather more experimental spectroscopic data available for PCl^+ than for NF^+ . The observation of chemiluminescence has been made from the reaction of PCl_3 with metastable $\text{Ar}(^3\text{P}_{2,0})$ atoms[29]. Long progressions of red-degraded bands were observed in the 400 - 600 nm region which were assigned to the $\text{A}^3\Pi_r \rightarrow \text{X}^3\Sigma^-$ system of PCl and a compact $\Delta\nu = 0$ sequence in the range 810 - 830 nm was assigned to the $\text{b}^1\Sigma \rightarrow \text{X}^3\Sigma^-$ transition of PCl .

The reactions of PCl_3 with discharged helium and metastable $\text{He}(^3\text{S})$ have been investigated by Coxon *et al.*[8]. A new visible system of red - degraded bands has been detected in the 400 - 690 nm region[8] and attributed to the emission spectrum of PCl^+ . Even if the bands of PCl^+ and those of $\text{PCl}(\text{A} \rightarrow \text{X})$ mentioned above are similar, the bands of PCl^+ are observed in different regions and were assigned to a $^2\Pi \rightarrow \text{X}^2\Pi$ transition of the diatomic cation PCl^+ . The vibrational parameters obtained by Coxon *et al.*[8] for two states were $\omega_e = 320.6 \text{ cm}^{-1}$ for the excited $^2\Pi$ state of PCl^+ and $\omega_e = 689.8 \text{ cm}^{-1}$, $\omega_e x_e = 2.60 \text{ cm}^{-1}$ for the $\text{X}^2\Pi$ ground state of PCl^+ .

Up to this point no rotational analyses had been made for the Group 5 monohalide cations except for five red-degraded bands of PF^+ [30].

In the subsequent studies of Coxon *et al.*[9] the first rotational spectroscopic analysis of the $\text{A}^2\Pi \rightarrow \text{X}^2\Pi$ system of PCl^+ has been made. With electronically excited PCl^+ produced from the reaction of PCl_3 with discharged helium an extensive band system

was observed over the range 400 - 700 nm. Rotational constants and equilibrium internuclear distances have been reported for these two states, namely

$B_e = 0.28437 \text{ cm}^{-1}$, $\alpha_e = 1.47 \times 10^{-3} \text{ cm}^{-1}$, $r_e = 0.1900 \text{ nm}$ for the $X^2\Pi$ state and

$B_0 = 0.18773 \text{ cm}^{-1}$, $B_1 = 0.18650 \text{ cm}^{-1}$, $r_e = 0.2334 \text{ nm}$ for the $A^2\Pi$ state.

There is no experimental information on other excited electronic states of PCl^+ . In view of this lack of information, we have performed calculations similar to those for NF^+ .

First, the asymptotic atomic states are either $\text{P} + \text{Cl}^+$ or $\text{P}^+ + \text{Cl}$.

Neutral phosphorus has three low lying states ^4S , ^2D and ^2P and the ground state is a ^4S . For the phosphorus cation there are three low lying states which are ^3P , ^1D and ^1S . The ^3P state is the ground state of this cation. The relative energy levels of two states are given in table 2.1. The experimental value for the ionization potential of P is 11.0 eV[27].

Atomic chlorine has only one valence state ^2P which is the ground state. For the cation there are three low lying states. The ground state is ^3P and the others are ^1D and ^1S . The table 2.2 gives details of the relative energies of the states. The experimental value of the ionization potential for Cl is 12.967 eV[27].

Second, to derive the form of the diatomic states of the ion PCl^+ two combinations have to be considered, namely $\text{Cl} + \text{P}^+$ and $\text{Cl}^+ + \text{P}$. The energies for the low lying states of the $\text{Cl} + \text{P}^+$ and $\text{Cl}^+ + \text{P}$ are given in table 2.2 and a correlation diagram describing the twelve possible combinations of $\text{Cl} + \text{P}^+$ and $\text{Cl}^+ + \text{P}$ is given in figure 2. All the electronic states in the correlation diagram can be generated using the Wigner-Witmer rules[28]. In this work for potential energy curves we have decided to consider the lowest dissociation asymptote $\text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P})$ in order to limit the number

of states to a manageable number. The following states correlating with the lowest dissociation asymptote $\text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P})$ can be obtained from the interpretation of the Wigner-Witmer rules as follows : $^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Delta$, $^2\Pi(2)$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Delta$, $^4\Pi(2)$.

For these states potential energy curves have been calculated using *ab initio* methods which are CASSCF and configuration interaction(CI) with three kinds of basis sets,namely vdz, vtz and vqz(valence quadruple-zeta) basis sets.

Table 2.1

Atomic energies of Cl and Cl⁺

Neutral state

Cl(²P) - 0 cm⁻¹(0 eV)

Cationic state

Cl⁺(³P) - 0 cm⁻¹(0 eV)

Cl⁺(¹D) - 11652 cm⁻¹(1.4448 eV)

Cl⁺(¹S) - 27900 cm⁻¹(3.4596 eV)

Atomic energies of P and P⁺

Neutral state

P(⁴S) - 0 cm⁻¹(0 eV)

P(²D) - 11361.7 cm⁻¹(1.4089 eV)

P(²P) - 18722 cm⁻¹(2.3215 eV)

Cationic state

P⁺(³P) - 0 cm⁻¹(0 eV)

P⁺(¹D) - 8882.6 cm⁻¹(1.1014 eV)

P⁺(¹S) - 21576.4 cm⁻¹(2.6754 eV)

Table 2.2

The twelve dissociation asymptotes are generated as follows.

Energy values are from Table 2.1

$$1) \text{P}(^4\text{S}) + \text{Cl}^+(^3\text{P}) = 0 \text{ cm}^{-1} + 0 \text{ cm}^{-1} = 0 \text{ cm}^{-1}(0 \text{ eV})$$

$$2) \text{P}(^4\text{S}) + \text{Cl}^+(^1\text{D}) = 0 \text{ cm}^{-1} + 11652 \text{ cm}^{-1} = 11652 \text{ cm}^{-1}(1.4448 \text{ eV})$$

$$3) \text{P}(^4\text{S}) + \text{Cl}^+(^1\text{S}) = 0 \text{ cm}^{-1} + 27900 \text{ cm}^{-1} = 27900 \text{ cm}^{-1}(3.4596 \text{ eV})$$

$$4) \text{P}(^2\text{D}) + \text{Cl}^+(^3\text{P}) = 11361.7 \text{ cm}^{-1} + 0 \text{ cm}^{-1} = 11361.7 \text{ cm}^{-1}(1.4089 \text{ eV})$$

$$5) \text{P}(^2\text{D}) + \text{Cl}^+(^1\text{D}) = 11361.7 \text{ cm}^{-1} + 11652 \text{ cm}^{-1} = 23013.7 \text{ cm}^{-1}(2.8537 \text{ eV})$$

$$6) \text{P}(^2\text{D}) + \text{Cl}^+(^1\text{S}) = 11361.7 \text{ cm}^{-1} + 27900 \text{ cm}^{-1} = 39261.7 \text{ cm}^{-1}(4.8684 \text{ eV})$$

$$7) \text{P}(^2\text{P}) + \text{Cl}^+(^3\text{P}) = 18722 \text{ cm}^{-1} + 0 \text{ cm}^{-1} = 18722 \text{ cm}^{-1}(2.3215 \text{ eV})$$

$$8) \text{P}(^2\text{P}) + \text{Cl}^+(^1\text{D}) = 18722 \text{ cm}^{-1} + 11652 \text{ cm}^{-1} = 30374 \text{ cm}^{-1}(3.7664 \text{ eV})$$

$$9) \text{P}(^2\text{P}) + \text{Cl}^+(^1\text{S}) = 18722 \text{ cm}^{-1} + 27900 \text{ cm}^{-1} = 46622 \text{ cm}^{-1}(5.7811 \text{ eV})$$

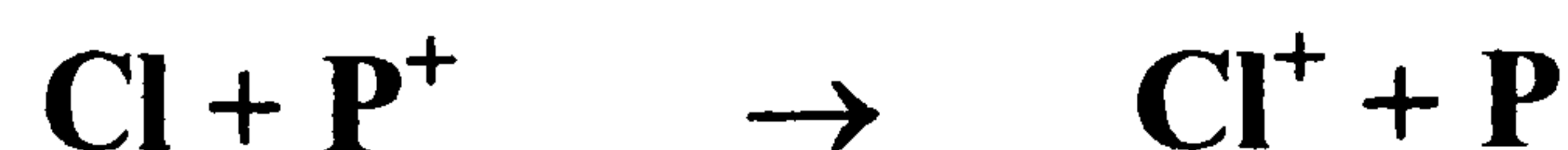
$$10) \text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P}) = 0 \text{ cm}^{-1} + 0 \text{ cm}^{-1} = 0 \text{ cm}^{-1}(0 \text{ eV})$$

$$11) \text{Cl}(^2\text{P}) + \text{P}^+(^1\text{D}) = 0 \text{ cm}^{-1} + 8882.6 \text{ cm}^{-1} = 8882.6 \text{ cm}^{-1}(1.1014 \text{ eV})$$

$$12) \text{Cl}(^2\text{P}) + \text{P}^+(^1\text{S}) = 0 \text{ cm}^{-1} + 21576.4 \text{ cm}^{-1} = 21576.4 \text{ cm}^{-1}(2.6754 \text{ eV})$$

$$\text{Cl(I) I.P(ionization Potential)} = 13.01 \text{ eV}$$

$$\text{P(I) I.P(ionization Potential)} = 11.0 \text{ eV}$$



$$\text{I.E(ionization Energy)} = \text{I.P(Cl)} - \text{I.P(P)} = 13.01 \text{ eV} - 11.0 \text{ eV} = 2.01 \text{ eV in energy}$$

Thus, the dissociation asymptote $\text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P})$ differs from the dissociation asymptote $\text{P}(^4\text{S}) + \text{Cl}^+(^3\text{P})$ by 2.01 eV. By the same method as used previously, if the energy of $\text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P})$ is defined as the zero of energy, the energy of $\text{P}(^4\text{S}) + \text{Cl}^+(^3\text{P})$ is 2.01 eV higher.

Therefore, an energy of **2.01 eV** is added to each energy level of the dissociation asymptotes(numbers 2 to 9 above) for **P + Cl⁺**.

The relative low lying energy levels are determined as follows

$$10) \text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P}) = 0 \text{ eV}$$

$$11) \text{Cl}(^2\text{P}) + \text{P}^+(^1\text{D}) = 1.1014 \text{ eV}$$

$$1) \text{P}(^4\text{S}) + \text{Cl}^+(^3\text{P}) = 0 \text{ eV} + 2.01 \text{ eV} = 2.01 \text{ eV}$$

$$12) \text{Cl}(^2\text{P}) + \text{P}^+(^1\text{S}) = 2.6754 \text{ eV}$$

$$4) \text{P}(^2\text{D}) + \text{Cl}^+(^3\text{P}) = 1.4089 \text{ eV} + 2.01 \text{ eV} = 3.4189 \text{ eV}$$

$$2) \text{P}(^4\text{S}) + \text{Cl}^+(^1\text{D}) = 1.4448 \text{ eV} + 2.01 \text{ eV} = 3.4548 \text{ eV}$$

$$7) \text{P}(^2\text{P}) + \text{Cl}^+(^3\text{P}) = 2.3215 \text{ eV} + 2.01 \text{ eV} = 4.3315 \text{ eV}$$

$$5) \text{P}(^2\text{D}) + \text{Cl}^+(^1\text{D}) = 2.8537 \text{ eV} + 2.01 \text{ eV} = 4.8637 \text{ eV}$$

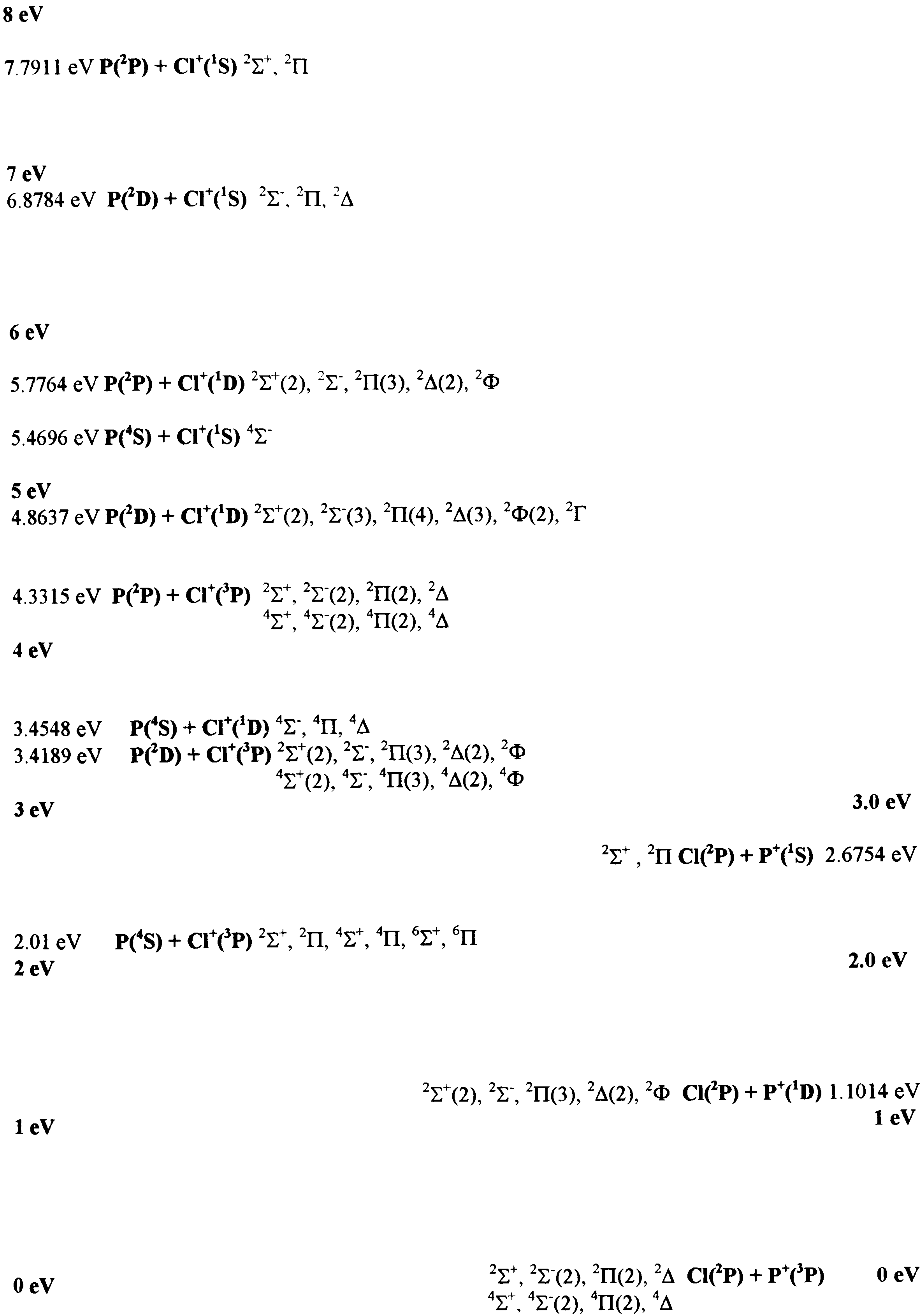
$$3) \text{P}(^4\text{S}) + \text{Cl}^+(^1\text{S}) = 3.4596 \text{ eV} + 2.01 \text{ eV} = 5.4696 \text{ eV}$$

$$8) \text{P}(^2\text{P}) + \text{Cl}^+(^1\text{D}) = 3.7664 \text{ eV} + 2.01 \text{ eV} = 5.7764 \text{ eV}$$

$$6) \text{P}(^2\text{D}) + \text{Cl}^+(^1\text{S}) = 4.8684 \text{ eV} + 2.01 \text{ eV} = 6.8784 \text{ eV}$$

$$9) \text{P}(^2\text{P}) + \text{Cl}^+(^1\text{S}) = 5.7811 \text{ eV} + 2.01 \text{ eV} = 7.7911 \text{ eV}$$

Figure 2. Correlation diagram for the low lying states of PCl^+



1.3 Introduction for AsCl⁺

The diatomic cation AsCl⁺ is similar to NF⁺ and PCl⁺ described earlier in two previous sections because it is one of the Group5 diatomic monohalide cations with 11 valence electrons. There is one difference compared to the last two sections in that we have moved from the first and second rows of the periodic table of the elements to an element from the third row of the periodic table. For several years attention has been focused on the rotational analyses of visible emission spectra of diatomic cations including 11 valence electrons. The rotational analysis of the A → X transition of AsCl⁺ was motivated from the discovery and vibrational analysis[31] of the spectrum at low resolution produced from the reaction of AsCl₃ with discharged helium. In the low resolution study of AsCl⁺ an extensive system of red-degraded bands observed in the range 4750 - 7700Å were assigned to A²Π → X²Π transition[33]. At medium resolution the visible A²Π → X²Π emission band system for AsCl⁺ has been observed in the range 5210 - 7215Å[33]. The rotational analysis of twelve ²Π_{1/2} -²Π_{1/2} sub bands of As³⁵Cl⁺ with ν'=0,1 and 14 ≤ ν'' ≤ 25 has been made[33]. Also for these two states spectroscopic parameters and the equilibrium internuclear distances have been obtained[33] which are $\omega_e = 527.00 \text{ cm}^{-1}$, $\omega_e x_e = 1.577 \text{ cm}^{-1}$, $B_e = 0.17140 \text{ cm}^{-1}$, $\alpha_e = 7.68 \times 10^{-4} \text{ cm}^{-1}$, $r_e = 2.031 \text{ Å}$ for X²Π and $B_0 = 0.11294 \text{ cm}^{-1}$, $B_1 = 0.11217 \text{ cm}^{-1}$, $r_e = 2.498 \text{ Å}$ for A²Π.

To our knowledge, there is no further information about the excited states of AsCl⁺. We would expect there to be some similarities with NF⁺ and PCl⁺. We have

performed a theoretical treatment using the same approach as before. As previous consideration of the atomic and diatomic energy levels has been made we do not report here the atomic states for Cl and Cl^+ because we have already given this information in the section 1.2.

For neutral arsenic (As) and arsenic cation(As^+), there are three low lying states each. The ground state of the neutral arsenic is ^4S . The other two atomic states are ^2D and ^2P . For As^+ , the ground state is ^3P and the excited valence states are ^1D and ^1P . The relative energies of these states are given in table 3.1. The experimental value for ionization potential of As is 9.81 eV[27].

To produce AsCl^+ two combinations must be considered, namely $\text{Cl} + \text{As}^+$ and $\text{Cl}^+ + \text{As}$. The relative energies of the low lying states for AsCl^+ are given in table 3.2 and a correlation diagram giving the twelve dissociation asymptotes is shown in figure 3. All the electronic states considered in the correlation diagram above are deduced from the Wigner - Witmer rules[28].

For this work we have considered the lowest dissociation asymptote $\text{Cl}(^2\text{P}) + \text{As}^+(^3\text{P})$, as in last two sections, for potential energy curves in order to keep the number of states considered manageable. Use of the Wigner-Witmer rules shows that the following states correlate with the dissociation asymptote $\text{Cl}(^2\text{P}) + \text{As}^+(^3\text{P})$:

$^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Delta$, $^2\Pi(2)$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Delta$, $^4\Pi(2)$.

There is one difference in our calculations for AsCl^+ from the two previous sections.

When we started calculations on AsCl^+ , compact basis sets for third row atoms were not available so we made sets of calculations with effective core potentials.

The valence electrons play a crucial role in chemical bonding and electrons from inner shells have little effect on chemical bonding. Thus, considering electrons from the

inner shells as part of the core to reduce the number of the two- electron integrals and considering only the valence electrons, we can make calculations for potential energy curves for a diatomic cation including heavier atoms as easily as the calculations for the small diatomic cations we have made previously. Also, we have made all electron calculations with the density matrix averaged atomic natural orbital basis sets of Pierloot et al[32]. For the states derived above potential energy curves have been calculated using CASSCF and configuration interaction(CI) with three sorts of basis sets, namely vdz, vtz, and vqz with the effective core potential method.

All electron calculations with CASSCF and CI have been made using the averaged atomic natural basis sets of Pierloot et al.

Table 3.1

Atomic energies for Cl and Cl⁺

As in as **Table 2.1**

Neutral state

Cl(²P) - 0 cm⁻¹ (0 eV)

Cationic state

Cl⁺(³P) - 0 cm⁻¹(0 eV)

Cl⁺(¹D) - 11652 cm⁻¹(1.4448 eV)

Cl⁺(¹S) - 27900 cm⁻¹(3.45 eV)

Atomic energies for As and As⁺

Neutral state

As(⁴S) - 0 cm⁻¹ (0 eV)

As(²D) - 10592.5 cm⁻¹ (1.3135 eV)

As(²P) - 18186.1 cm⁻¹ (2.2551 eV)

Cationic state

As⁺(³P) - 0 cm⁻¹ (0 eV)

As⁺(¹D) - 10093 cm⁻¹ (1.2515 eV)

As⁺(¹S) - 225930 cm⁻¹ (2.8015 eV)

Table 3.2

The twelve dissociation asymptotes are as follows

- 1) $\text{As}(^4\text{S}) + \text{Cl}^+(^3\text{P}) = 0 \text{ eV} + 0 \text{ eV} = 0 \text{ eV}$
- 2) $\text{As}(^4\text{S}) + \text{Cl}^+(^1\text{D}) = 0 \text{ eV} + 1.4448 \text{ eV} = 1.4448 \text{ eV}$
- 3) $\text{As}(^4\text{S}) + \text{Cl}^+(^1\text{S}) = 0 \text{ eV} + 3.4596 \text{ eV} = 3.4596 \text{ eV}$
- 4) $\text{As}(^2\text{D}) + \text{Cl}^+(^3\text{P}) = 1.3135 \text{ eV} + 0 \text{ eV} = 1.3135 \text{ eV}$
- 5) $\text{As}(^2\text{D}) + \text{Cl}^+(^1\text{D}) = 1.3135 \text{ eV} + 1.4448 \text{ eV} = 2.7583 \text{ eV}$
- 6) $\text{As}(^2\text{D}) + \text{Cl}^+(^1\text{S}) = 1.3135 \text{ eV} + 3.4596 \text{ eV} = 4.7731 \text{ eV}$
- 7) $\text{As}(^2\text{P}) + \text{Cl}^+(^3\text{P}) = 2.2551 \text{ eV} + 0 \text{ eV} = 2.2551 \text{ eV}$
- 8) $\text{As}(^2\text{P}) + \text{Cl}^+(^1\text{D}) = 2.2551 \text{ eV} + 1.4448 \text{ eV} = 3.6999 \text{ eV}$
- 9) $\text{As}(^2\text{P}) + \text{Cl}^+(^1\text{S}) = 2.2551 \text{ eV} + 3.4596 \text{ eV} = 5.7147 \text{ eV}$
- 10) $\text{Cl}(^2\text{P}) + \text{As}^+(^3\text{P}) = 0 \text{ eV} + 0 \text{ eV} = 0 \text{ eV}$
- 11) $\text{Cl}(^2\text{P}) + \text{As}^+(^1\text{D}) = 0 \text{ eV} + 1.2515 \text{ eV} = 1.2515 \text{ eV}$
- 12) $\text{Cl}(^2\text{P}) + \text{As}^+(^1\text{S}) = 0 \text{ eV} + 2.8015 \text{ eV} = 2.8015 \text{ eV}$

Cl(I) I.P(Ionization Potential) = 13.01 eV

As(I) I.P(Ionization Potential) = 9.81 eV



$$\text{I.E(Ionization Energy)} = \text{I.P(Cl)} - \text{I.P(As)} = 13.01 \text{ eV} - 9.81 \text{ eV} = 3.2 \text{ eV}$$

in energy. Thus, the dissociation asymptote $\text{Cl}^+(^3\text{P}) + \text{As}(^4\text{S})$ is 3.2 eV higher than the dissociation asymptote $\text{Cl}(^2\text{P}) + \text{As}^+(^3\text{P})$.

If the energy level of $\text{Cl}(^2\text{P}) + \text{As}^+(^3\text{P})$ is taken as the zero of energy, the energy of $\text{Cl}^+(^3\text{P}) + \text{As}(^4\text{S})$, number 1 above, lies 3.2 eV higher.

An energy of **3.2 eV** is added to each of the energies for **Cl⁺ + As** (numbers 2 to 9 shown above).

The relative low-lying energy states derived from the definition above are given below.

$$10) \text{Cl}(^2\text{P}) + \text{As}^+(^3\text{P}) = 0 \text{ eV}$$

$$11) \text{Cl}(^2\text{P}) + \text{As}^+(^1\text{D}) = 1.2515 \text{ eV}$$

$$12) \text{Cl}(^2\text{P}) + \text{As}^+(^1\text{S}) = 2.8015 \text{ eV}$$

$$1) \text{As}(^4\text{S}) + \text{Cl}^+(^3\text{P}) = 0 \text{ eV} + 3.2 \text{ eV} = 3.2 \text{ eV}$$

$$4) \text{As}(^2\text{D}) + \text{Cl}^+(^3\text{P}) = 1.3135 \text{ eV} + 3.2 \text{ eV} = 4.5135 \text{ eV}$$

$$2) \text{As}(^4\text{S}) + \text{Cl}^+(^1\text{D}) = 1.4448 \text{ eV} + 3.2 \text{ eV} = 4.6448 \text{ eV}$$

$$7) \text{As}(^2\text{P}) + \text{Cl}^+(^3\text{P}) = 2.2551 \text{ eV} + 3.2 \text{ eV} = 5.4551 \text{ eV}$$

$$5) \text{As}(^2\text{D}) + \text{Cl}^+(^1\text{D}) = 2.7583 \text{ eV} + 3.2 \text{ eV} = 5.9583 \text{ eV}$$

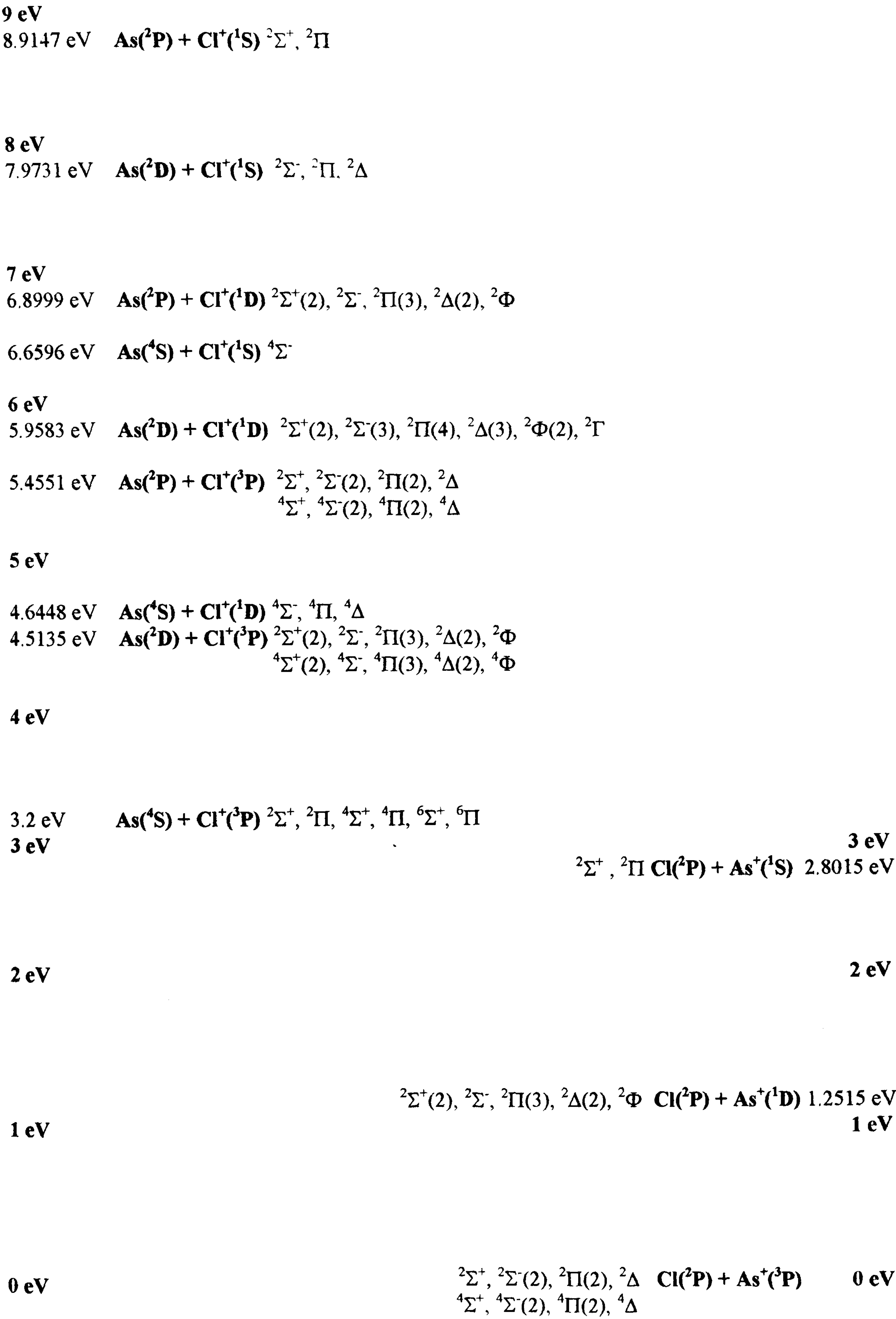
$$3) \text{As}(^4\text{S}) + \text{Cl}^+(^1\text{S}) = 3.4596 \text{ eV} + 3.2 \text{ eV} = 6.6596 \text{ eV}$$

$$8) \text{As}(^2\text{P}) + \text{Cl}^+(^1\text{D}) = 3.6999 \text{ eV} + 3.2 \text{ eV} = 6.8999 \text{ eV}$$

$$6) \text{As}(^2\text{D}) + \text{Cl}^+(^1\text{S}) = 4.7731 \text{ eV} + 3.2 \text{ eV} = 7.9731 \text{ eV}$$

$$9) \text{As}(^2\text{P}) + \text{Cl}^+(^1\text{S}) = 5.7147 \text{ eV} + 3.2 \text{ eV} = 8.9147 \text{ eV}$$

Figure 3. Correlation diagram for the low lying states of AsCl⁺



1.4 Introduction for BBr^+

As well as being important in spectroscopy, the development of new molecular ion spectra can contribute to some other fields, for instance, astrophysics or ion-molecule reactions in discharge plasma. Most of the diatomic cation studies on emission spectra have been carried out with electric-discharge, electron-impact and ion-impact sources. Following the discovery of the flowing afterglow optical spectroscopy, emission spectra have been obtained from diatomic cations. With the help of this valuable new technique a number of new UV and visible emission spectra of the Group 4 and Group 5 monohalide diatomic cations have been discovered as follows[35]:

$\text{CCl}^+(\text{A}^1\Pi^1 - \text{X}^1\Sigma^+, {}^3\Pi - \text{X}^1\Sigma^+)$ [37], $\text{SiCl}^+(\text{a}^3\Pi_r - \text{X}^1\Sigma^+)$ [38], $\text{GeCl}^+(\text{a}^3\Sigma^+ - \text{X}^1\Sigma^+)$ [39], $\text{SnCl}^+(\text{a}^3\Sigma^+ - \text{X}^1\Sigma^+)$ [40], $\text{CBr}^+(\text{a}^3\Pi_r - \text{X}^1\Sigma^+)$ [41,42], $\text{SiBr}^+(\text{a}^3\Pi_r - \text{X}^1\Sigma^+)$ [43], $\text{PCl}^+(\text{A}^2\Pi - \text{X}^2\Pi)$ [8], and $\text{AsCl}^+(\text{A}^2\Pi - \text{X}^2\Pi)$ [31].

The Group 6 monohalide diatomic cations such as $\text{O}_2^+(\text{A}^2\Pi - \text{X}^2\Pi)$ [2], $\text{SO}^+(\text{A}^2\Pi - \text{X}^2\Pi)$ [3-5], $\text{SeO}^+(\text{A}^2\Pi - \text{X}^2\Pi)$ [6], $\text{S}_2^+(\text{A}^2\Pi - \text{X}^2\Pi)$ [34] mentioned in the section 1.1 have been identified from photoelectron spectroscopy.

As shown above and in the three previous sections 1.1,1.2 and 1.3, the Group 4, Group5 and Group6 monohalide diatomic cations have been investigated relatively well. However, little information has been obtained for the Group 3 monohalide diatomic cations. Spectroscopic studies on the Group 3 monohalide diatomic cations have been made by Glenewinkel - Meyer *et al* [36]. and Yamaguchi *et al* [35].

Chemiluminescent ion-molecule reactions of A^+ with X_2 at low (2 - 10eV_{CM}) kinetic energy in a beam gas arrangement have been performed to produce electronically

excited species AX^+ with $A = B, Al, Ga, In$ and $X = F, Cl, Br$ [36]. Except for BCl^+ and BBr^+ optical spectra for 10 out of the 12 possible combinations AX^+ have been observed in the 2000 - 6000 Å region.

A total of 18 new band systems have been found. Three types of band systems have been observed.

First, in all combinations excluding BCl^+ and BBr^+ a very broad quasicontinuum has been observed with undulatory structure. On the basis of electronic state correlation discussions, photoelectron data and some *ab initio* calculations these band systems have been assigned to $B^2\Sigma^+ - X^2\Sigma^+$ transitions. It has been assumed that the minima of the $B^2\Sigma^+$ excited state potential energy curves occur at considerably longer distances than for the $X^2\Sigma^+$ ground states in order to interpret the breadth of the observed spectra. This interpretation is supported by the *ab initio* calculations for AlF^+ and $AlCl^+$ by Glenewinkel-Meyer et al[44] and for GaF^+ and $GaCl^+$ by Yoshikawa and Hirst[45]. These calculations have also shown that the long bond lengths for the $B^2\Sigma^+$ states are derived from avoided intersections between potential curves correlating with the first two dissociation asymptotes, $A^+(^1S) + X(^2P)$ and $A^+(^3P) + X(^2P)$.

Second, for six species AX^+ , narrow band systems have been detected in the 2500Å region. They have been characterized as $C^2\Pi - X^2\Sigma^+$ transitions from comparison with the systematics of the similar $A^2\Pi - X^2\Sigma^+$ transitions for the isoelectronic alkaline earth halides for which there is resolved fine structure and with the aid of *ab initio* calculation.

Third, for the $GaCl^+$, $GaBr^+$, and $InBr^+$ spectra, there are narrow features in addition to

the C - X transition. They are assigned to $D^2\Sigma^+ - X^2\Sigma^+$ transitions, similar to the alkaline earth halide $B^2\Sigma^+ - X^2\Sigma^+$ band systems. BBr^+ also includes a third row atom, as in the case of $AsCl^+$. In the chemiluminescence study of Glenewinkel-Meyer *et al* there was no broad quasi-continuum attributable to a $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition.

Emission spectra of BBr_3 from the reaction of He with Ar afterglows have been observed in the 470 - 515nm region and a new visible band system has been assigned to the $A^2\Pi_r - X^2\Sigma^+$ transition of BBr^+ by Yamaguchi *et al* [35]. The spectroscopic parameters have been reported from the vibrational analysis and are $\omega_e = 813.8 \text{ cm}^{-1}$, $\omega_e x_e = 7.5 \text{ cm}^{-1}$ for the excited $A^2\Pi_r$ state of BBr^+ and $\omega_e = 761.5 \text{ cm}^{-1}$, $\omega_e x_e = 6.3 \text{ cm}^{-1}$ for the $X^2\Sigma^+$ ground state of BBr^+ .

The diatomic cation BBr^+ is different from the other AX^+ species considered by Glenewinkel-Meyer *et al* [36]. The second dissociation asymptote $B(^2P) + Br(^3P)$ is 3.54eV higher than the first dissociation asymptote $B(^1S) + Br(^2P)$. In contrast, $B(^3P) + Br(^2P)$ lies 4.63eV higher. Therefore, it is expected that the potential energy curves for BBr^+ will be quite different from those for the ten other AX^+ species. Glenewinkel-Meyer *et al* [36] expressed doubts about the spectroscopic analysis of Yamaguchi *et al* [35]. Many $^2\Pi_r - X^2\Sigma^+$ transitions have been observed [36] and assigned to $C^2\Pi_r - X^2\Sigma^+$ respectively and the $^2\Pi_r$ state has been attributed to the second $^2\Pi$ state(upper state) named $C^2\Pi$. The observed (C-X) transitions show increasing blue shifts in the order $X = F, Cl, Br$ and the (C-X) transition for BBr^+ would be expected to be located at 300nm or less compared to the wavelength range, 470nm-515nm, observed by Yamaguchi *et al*[35].

Moreover, from the approximate dissociation energies, D_e , obtained from the ω_e and $\omega_e x_e$ values of Yamaguchi *et al* it is argued that a transition between the $X^2\Sigma^+$ state and a $^2\Pi$ state correlating with $B(^2P) + Br^+(^3P)$ would have a T_e value of about 3.66eV[36] compared to the value of 2.50eV reported by Yamaguchi *et al* [35].

As usual, in view of the lack of the information available we thought it would be worthwhile to make our calculations.

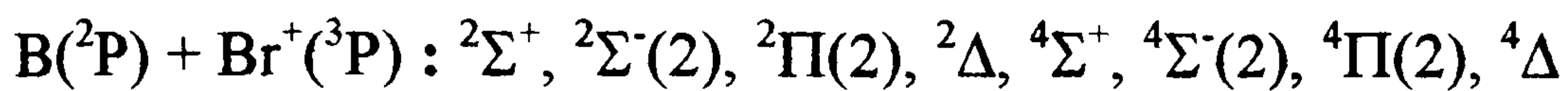
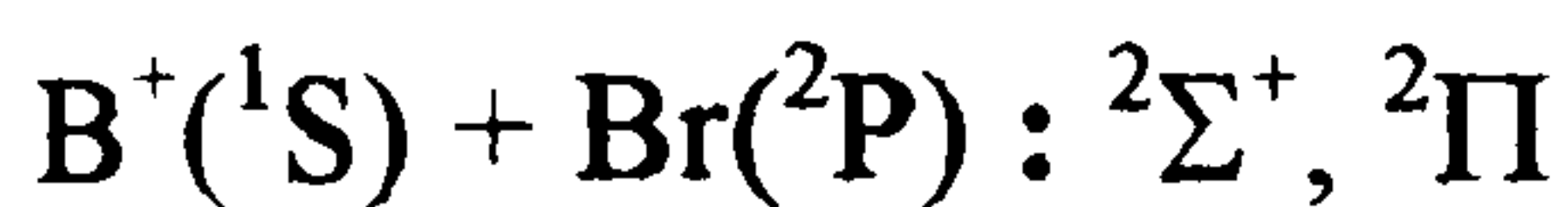
For our work the interpretation of the atomic and diatomic energy levels has been considered by methods outlined above.

First of all, atomic states are divided into two pairs which are either neutral bromine(Br) and boron cation(B^+) or bromine cation(Br^+) and neutral boron(B).

In the case of Br and Br^+ , atomic bromine has one valence state 2P , which is the ground state. For bromine cation there are two low lying states 3P and 1D and 3P is the ground state. The 1S state is higher in energy. The relative energies of these two states are shown in table 4.1. The experimental value of the ionization potential for Br is 11.84eV[27]. In the case of B and B^+ , for B there is one valence state 2P , which is the ground state. For B^+ there are three low lying states which are 1S , 3P and 1P of which 1S is the ground state. The relative energy levels of these two states B and B^+ are given in table 4.1. The experimental value for ionization potential of B is 8.296eV[27].

Secondly, to produce the diatomic ion BBr^+ two combinations should be taken into account, namely $B^+ + Br$ and $B + Br^+$. The relative energies for the low lying states of $B^+ + Br$ and $B + Br^+$ are given in table 4.2 and a correlation diagram showing the five dissociation asymptotes is given in figure 4.

All the electronic states shown in a correlation diagram are generated from the Wigner-Witmer rules[28]. In this work we have considered the two lowest dissociation asymptotes, namely $B^+(^1S) + Br(^2P)$ and $B(^2P) + Br^+(^3P)$ for calculations of potential energy curves in order to keep the number of the states manageable. The interpretation of the Wigner-Witmer rules gives the following states which correlate with the dissociation asymptotes mentioned above as follows.



For the states given above the calculation of potential energy curves have been carried out using CASSCF and CI with three kinds of basis sets, namely vdz, vtz and vqz in the effective core potential method. Also, all electron calculation *ab initio* methods have been made with the density matrix averaged atomic natural orbital spd basis sets of Pierloot et al[32].

Table 4.1

Atomic energies of Br and Br⁺

Neutral state

Br(²P) - 0 cm⁻¹(0 eV)

Cationic state

Br⁺(³P) - 0 cm⁻¹(0 eV)

Br⁺(¹D) - 11409 cm⁻¹(1.4147 eV)

Atomic energies for B and B⁺

Neutral state

B(²P) - 0 cm⁻¹(0 eV)

Cationic state

B⁺(¹S) - 0 cm⁻¹(0 eV)

B⁺(³P) - 37333.6 cm⁻¹(4.6294 eV)

B⁺(¹P) - 73396.7 cm⁻¹(9.1012 eV)

Table 4.2

The low-lying states of BBr⁺ are derived from the possible combinations

- 1) Br⁺(³P) + B(²P) = 0 cm⁻¹ + 0 cm⁻¹ = 0 cm⁻¹(0 eV)
- 2) Br⁺(¹D) + B(²P) = 11409 cm⁻¹ + 0 cm⁻¹ = 11409 cm⁻¹(1.4147 eV)
- 3) Br(²P) + B⁺(¹S) = 0 cm⁻¹ + 0 cm⁻¹ = 0 cm⁻¹(0 eV)
- 4) Br(²P) + B⁺(³P) = 0 cm⁻¹ + 37333.6 cm⁻¹ = 37333.6 cm⁻¹(4.6294 eV)
- 5) Br(²P) + B⁺(¹P) = 0 cm⁻¹ + 73396.7 cm⁻¹ = 73396.7 cm⁻¹(9.1012 eV)

Br(I) I.P(Ionization Potential) 11.84 eV

B(I) I.P(Ionization potential) 8.296 eV



$$\mathbf{I.E (Ionization Energy) = I.P(Br) - I.P(B) = 11.84\ eV - 8.296\ eV = 3.544\ eV}$$

Thus, there is an energy difference of **3.544 eV** between the energy levels of the two dissociation asymptotes **Br(²P) + B⁺(¹S)** and **Br⁺(³P) + B(²P)**.

By the same method as before the energy level of **Br(²P) + B⁺(¹S)** is taken as the zero of energy and the energy level of **Br⁺(³P) + B(²P)** ,(number 1 above) is **3.544 eV** higher. Also adding an energy of **3.544 eV** to the energy of the dissociation asymptote **Br⁺(¹D) + B(²P)** (number 2 shown above) the relative energy level for **Br⁺(¹D) + B(²P)** is **4.959 eV**.

The relative energy states are obtained from the above definition.

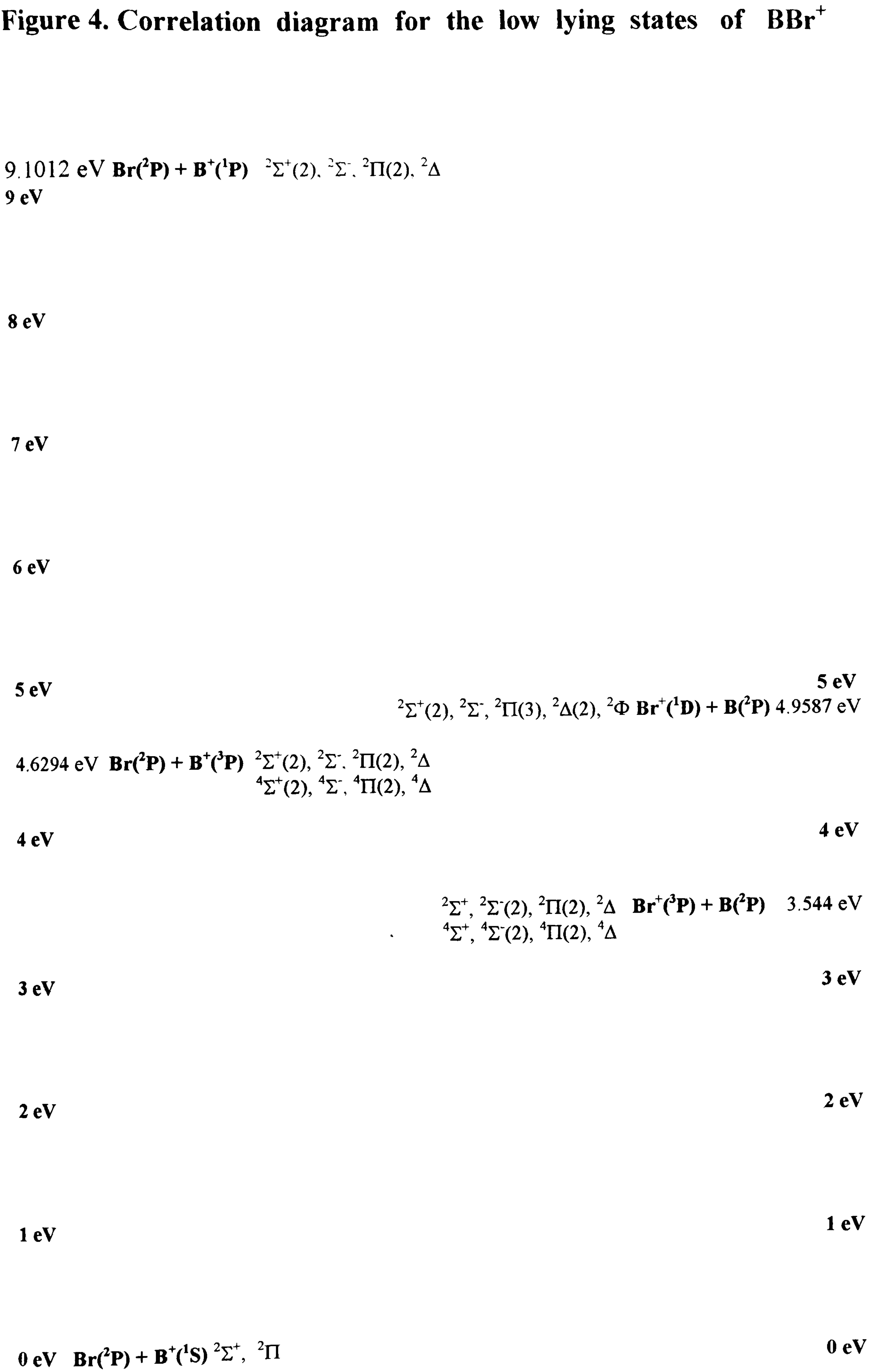
$$3) \mathbf{Br(^2P) + B^+(^1S) = 0\ eV}$$

$$1) \mathbf{Br^+(^3P) + B(^2P) = 0\ eV + 3.544\ eV = 3.544\ eV}$$

$$4) \mathbf{Br(^2P) + B^+(^3P) = 4.6294\ eV}$$

$$2) \mathbf{Br^+(^1D) + B(^2P) = 1.4147\ eV + 3.544\ eV = 4.9587\ eV}$$

$$5) \mathbf{Br(^2P) + B^+(^1P) = 9.1012\ eV}$$

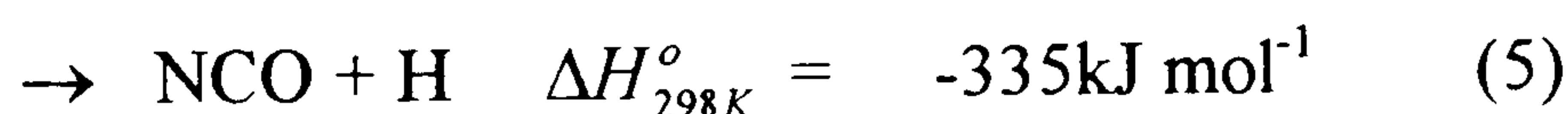
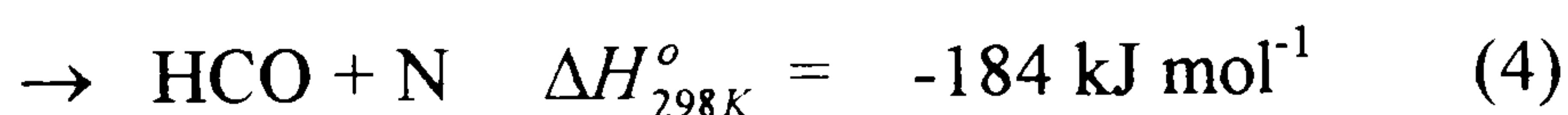
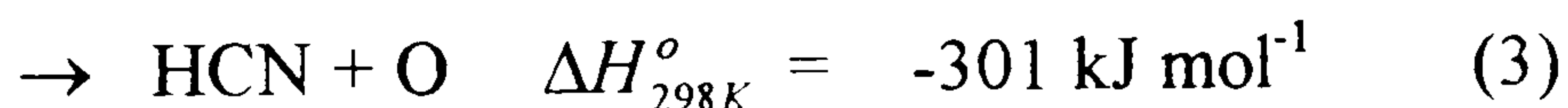
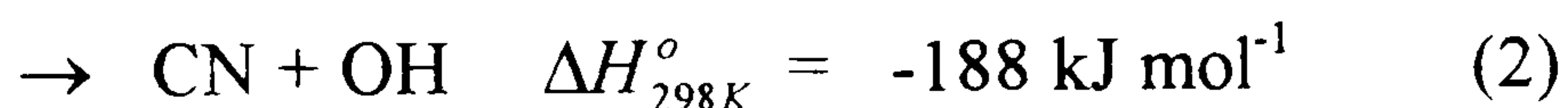
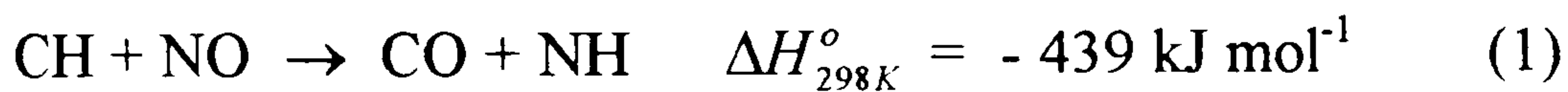


1.5 Introduction for HC + NO

The CH radical is highly reactive and is found in a wide variety of environments [74,78]. The reaction of methylidyne with nitrogen molecules is important in combustion chemistry [80-83] and in the chemistry of planetary atmospheres [84] and its significance for fundamental studies [85-92] is of continuing interest [73]. Also, the kinetics of the reactions with CH are of great interest in combustion chemistry [74,79]. It is believed that the methylidyne radical (CH) plays an important role in the formation of prompt NO_x or electronically excited and ionic species in combustion systems due to its high heat of formation and reactivity [75]. It has been thought that the reaction of the CH with N_2 , generating $\text{N} + \text{HCN}$ at high temperatures, is the source of “prompt” NO [74,75,102,103], and also it has been proposed that the reaction of NO with CH is one of the most important reactions in flames [104] including nitrogen compounds.

The reactions of CH are the key to understanding the chemistry of planetary atmospheres, in particular, in the nitrogen and hydrocarbon-rich atmosphere of Titan [84], and those of Jupiter and Neptune [93]. Maybe CH reactions might play an important role in interstellar clouds [94] and also are of basic interest because there are many exit channels as shown below, leading to the formation of electronically excited states. Reactions of CH with diatomics may proceed as prototypical four-atom reactions. In various environments over a very wide range of temperatures CH reactions may be of significance. Combustion temperatures can rise up to 1000 K and more, while temperatures from 70 K to 170 K are typical of the atmospheres of extraterrestrial planets, namely Titan and Jupiter [95]. Extremely low temperatures in the range 10 - 50 K (and densities in the range $10^3 - 10^6 \text{ cm}^{-3}$) are general in dense

interstellar clouds [96]. To understand the role of CH and the relative significance of CH reactions in such different environments and to better understand its high reactivity it is desirable to study the kinetics of the reactions of CH over as wide a range of temperatures as possible. Rate coefficients for the kinetics of CH reactions with NO have been reported in the range $T = 13 - 708 \text{ K}$ [74]. Detailed investigations for CH radicals in hydrocarbon/air flames have already been carried out with laser absorption [99] and laser-induced fluorescence(LIF) [100] methods for the ground state of CH, and with the emission spectroscopy [99,101] for the electronically excited state. The reaction of CH with NO, as first examined by Lin [105], has many possible exothermic reaction channels as follows [85(a)].



Reaction products have not been identified, but there are many products which are thermochemically possible. Even though the rate parameters for the total consumption for CH on reaction with a wide range of stable molecules have been measured [111], the reaction mechanisms have not been determined definitively. Since there is no direct experimental information about the major products from the reaction of CH with NO, further investigation of these reactions is of interest in order to compare with various predictions. Moreover, quantum mechanical calculations

have been performed in order to identify the mechanisms for these reactions. No previous studies have been made for the rate constant for the reaction of vibrationally excited CH with NO. Thus, as suggested above calculations of the potential energy surface of the CHNO isomers have been carried out with the ab initio molecular orbital method [76,77].

Among the 38 possible CHNO isomers [76], there are six bound cases [77], namely HNCO, HOCN, HCNO(fulminic acid), HONC, HNOC, and HCON.

Only two isomers HNCO [106] and HCNO [107], which are of astrophysical interest, have been studied spectroscopically. With the methods of high resolution rotational and vibrational spectroscopy, both of them have been studied over the past 25 years. Much useful information has been obtained concerning their structures, electric moments, physical properties and potential energy surfaces in a number of spectroscopic investigations of the two isomers [77] (especially for HCNO [112-135]). A number of studies have been made to identify their geometries [76,108-110]. However, from the experimental investigations of the structures of HOCN and HCNO, in particular HCNO, it remains to be confirmed experimentally whether the molecular structures are linear or slightly bent for the heavy-atom chains [77]. Also, the substitution studies cannot distinguish between a linear or a slightly bent NCO chain in the structures HOCN and HCNO because the N, C and O atoms are located very close to the principal axis α , and make very little contribution to the moment of inertia I_a . Furthermore, from the assumption of a linear heavy atom chain, the location of the H atom is unclear. This is because the zero-point vibrational effects are present when hydrogen is replaced by deuterium, due to the anharmonicity of the potential in the large-amplitude HNC bending vibration. Several of these species are of interest,

particularly HCNO, because they are quasilinear. The properties of a quasilinear molecule depend on a low-lying, large amplitude bending mode having a rather anharmonic bending potential. For such a molecule, the bending motion and the rotation about the axis of least moment of inertia, the α axis, are strongly coupled. If the molecule is regarded as being linear, it has two rotational degrees of freedom and $3N - 5$ vibrational degrees of freedom whereas if the molecule is bent, it has three rotational degrees of freedom and $3N - 6$ vibrational degrees of freedom. Thus, on going from the linear case to the bent case a vibrational degree of freedom becomes a rotational degree of freedom. This description implies that the molecule should be considered to be non-rigid, which means that it is neither linear nor bent. The potential energy surface of CHNO has been studied by Poppinger, Radom and Pople[76]. It was concluded that HNCO, HOCN, HCNO and HONC can all be isolated. The importance of their calculations [76] with *ab initio* methods was to investigate the in-plane angular dependence of the surface near HNCO, HCNO and HONC. It was very flat and thus, very anharmonic and it was determined that especially HNCO and HCNO were quasilinear. In recent years HOCN and HONC have been investigated in matrix isolation experiments[108,136]. From the previous *ab initio* theoretical studies of the CHNO isomers[76], HCNO is less stable than HOCN which is less stable than HNCO. The calculated energetics imply that HONC is sufficiently stable for it to be isolated. Both HNCO and HCNO have been detected in the gas phase.

In the work by Pinnavaia *et.al.* [77] large basis sets have been used to determine the quadratic force field and the effects of electron correlation allowed for by the MP2 method. All the calculations have considered two sorts of basis sets, namely

DZP(double-zeta plus polarization)[137,138] and TZ2P(triple-zeta plus double polarization)[138,139]. Initially, the atomic contracted Gaussian basis sets may be defined as C(9s5p1d/4s2p1d), N(9s5p1d/4s2p1d), O(9s5p1d/4s2p1d) and H(4s1p/2s1p). The polarization function orbital exponents were $\alpha_d(\text{C}) = 0.8$, $\alpha_d(\text{N}) = 0.8$, $\alpha_d(\text{O}) = 0.9$ and $\alpha_p(\text{H}) = 1.0$. Secondly, the TZ2P basis sets were the C(10s6p/5s4p), N(10s6p/5s4p), O(10s6p/5s4p) and H(6s/3s) triple-zeta contractions of Huzinaga primitives. The polarization exponents used were $\alpha_d(\text{C}) = 1.2, 0.4$, $\alpha_d(\text{N}) = 1.35, 0.45$, $\alpha_d(\text{O}) = 1.35, 0.45$ and $\alpha_p(\text{H}) = 1.5, 0.5$. For HCNO, f basis sets were assigned to C, N and O with the exponent 1.0 respectively.

These basis sets were used in Møller-Plesset second order perturbation theory(MP2) correlating all electrons. Also, analytical gradients and second derivatives may be generated from the MP2 calculation [140]. Even though the MP2 method is not too complicated, it is size-consistent and can give very accurate geometry and force-constant predictions [141], showing that it is a very valuable method for calculating harmonic force constants of polyatomic molecules [97,98].

For our work we have calculated the potential energy surface for HC + NO using *ab initio* methods (CASSCF + CI) with VDZ basis sets for four states $^1\Sigma^+(2)$, $^3\Sigma^+(2)$, $^1\Sigma^-(2)$ and $^3\Sigma^-(2)$ for linear geometries and $^1A'(2)$ state for bent geometries, respectively keeping the number of states limited manageable.

In these calculations we have imposed some limitations on the possible configurations considered in order to reduce the computational difficulty: In addition to the 1s orbitals on C, N and O being frozen in the CI calculation, the 2s orbitals are also frozen.

2. *Ab Initio* Molecular Orbital Theory

2.1 The Born-Oppenheimer separation and potential energy surfaces

2.1.1 Introduction

The major problem in the treatment molecular structure is that the electronic motion should be separated from the nuclear motion because the nuclei are much heavier than the electrons and therefore the nuclei move more slowly than the electrons. This idea leads to the Born-Oppenheimer separation from which one obtains the concept of a potential energy surface. For a diatomic molecule, the potential energy surface is expressed in terms of a function of the internuclear distance and this is called the potential energy curve for a diatomic molecule.

2.1.2 Theory

Quantum mechanics [142] can enable one to calculate the energy and many properties of a stationary state of a molecule by solving the Schrödinger partial differential equation given as follows,

$$H\Psi = E\Psi \quad (2.1.1)$$

where H is expressed as the Hamiltonian, a differential operator giving the total energy and the numerical factor on the right side is the energy E, which is the eigenvalue of the operator, and Ψ is the wavefunction called the eigenfunction.

The Hamiltonian H is defined as the sum of kinetic and potential energies,

$$H = T + V \quad (2.1.2)$$

The kinetic energy T is given as a sum of differential operators,

$$T = -\frac{h^2}{8\pi^2} \sum_i \frac{1}{m_i} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \quad (2.1.3)$$

Here the sum is over all particles i which are nuclei and electrons, m_i represents the mass of particle i and h is *Planck's constant*.

The potential energy V is given by the coulomb interaction,

$$V = \sum_{i < j} \sum \left(\frac{e_i e_j}{r_{ij}} \right) \quad (2.1.4)$$

where the sum is over distinct pairs of particles (i, j) which have electric charges e_i, e_j separated by a distance r_{ij} . For electrons $e_i = -e$ and for a nucleus of atomic number Z_i , $e_i = +Z_i e$.

Firstly if the quantum mechanical problem for the electron motion with the nuclei fixed is considered, one obtains an effective electronic energy $E^{\text{eff}}(\mathbf{R})$ which depends on the relative nuclear coordinates, defined by \mathbf{R} . For a diatomic molecule, only the internuclear distance, R , is needed and $E^{\text{eff}}(\mathbf{R})$ describes the potential curve for the molecule. On the other hand, for the polyatomic molecules, more relative coordinates are required and $E^{\text{eff}}(\mathbf{R})$ is interpreted as the potential surface for the molecule. As mentioned above, the separation of the nuclear and electronic motions is usually named the Born-Oppenheimer approximation which is quantitatively defined by solving the Schrödinger equation for electrons in the field of fixed nuclei,

$$H^{\text{elec}} \Psi^{\text{elec}}(\mathbf{r}, \mathbf{R}) = E^{\text{eff}}(\mathbf{R}) \Psi^{\text{elec}}(\mathbf{r}, \mathbf{R}). \quad (2.1.5)$$

Ψ^{elec} is the electronic wavefunction which depends on the electronic coordinates, \mathbf{r} , and the nuclear coordinates, \mathbf{R} . The electronic Hamiltonian, H^{elec} , describes the motion of electrons only in the field of fixed nuclei and is given by

$$H^{\text{elec}} = T^{\text{elec}} + V. \quad (2.1.6)$$

where T^{elec} is the electronic kinetic energy expressed as follows,

$$T^{\text{elec}} = -\left(\frac{h^2}{8\pi^2 m}\right) \sum_i^{\text{electrons}} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \quad (2.1.7)$$

and V is the coulomb potential energy given below,

$$V = - \sum_i^{\text{electrons}} \sum_s^{\text{nuclei}} \frac{Z_s e^2}{r_{is}} + \sum_{i,j}^{\text{electrons}} \frac{e^2}{r_{ij}} + \sum_{s<t}^{\text{nuclei}} \frac{Z_s Z_t e^2}{R_{st}} \quad (2.1.8).$$

The first part of the coulomb potential energy gives the electron-nuclear attraction.

The second corresponds to electron-electron repulsion and the third to nuclear-nuclear repulsion which is independent of the electronic coordinates and is a constant contribution to the energy. The potential energy surface, $E^{\text{eff}}(\mathbf{R})$ is the key to understanding the quantitative description of chemical structures and reaction processes. The ground-state potential energy surface $E^{\text{eff}}(\mathbf{R})$ is obtained from the lowest-energy solution of the electronic Schrödinger equation. If $E^{\text{eff}}(\mathbf{R})$ is explored as a function of \mathbf{R} , generally $E^{\text{eff}}(\mathbf{R})$ will have a number of local minima. These are all equilibrium structures.

If several distinct potential minima are allowed, the molecule possesses a number of isomeric forms. Furthermore, the potential surface may also include saddle points which are called stationary points where the energy is a maximum for one or more orthogonal directions. If the second derivative matrix of E with respect to nuclear coordinates has one negative eigenvalue at such a point, then that point is a transition state for a chemical reaction defined as the point at which the maximum energy on a path connecting two minima on the potential surface is lowest.

For the electronic Schrödinger equation (2.5) it is useful to remove the universal constants and to introduce atomic units where the unit of mass, the unit of charge, the unit of length and the unit of energy are changed to the mass of electron, the charge on

the electron, the bohr (a_0) and the energy (E_h), respectively. The definition of the Bohr radius, a_0 , is

$$a_0 = \frac{h^2}{(4\pi^2 m e^2)} \quad (2.1.9)$$

Therefore, new coordinates (x', y', z') can be derived:

$$x' = \frac{x}{a_0} \quad (2.1.10)$$

Similarly, the hartree (E_h) is defined as shown below

$$E_h = \frac{e^2}{a_0} \quad (2.1.11)$$

Thus, new energies (E') are produced as follow

$$E' = \frac{E}{E_h} \quad (2.1.12)$$

If new coordinates (2.1.10) and new energies (2.1.12) are inserted to the Schrödinger equation (2.1.5), the following equation (2.1.13) is generated:

$$H'\Psi' = E'\Psi' \quad (2.1.13)$$

Here, the Hamiltonian, H' , in atomic units is represented by (2.1.14) below

$$H' = -\frac{1}{2} \sum_i^{electrons} \left(\frac{\partial^2}{\partial x_i'^2} + \frac{\partial^2}{\partial y_i'^2} + \frac{\partial^2}{\partial z_i'^2} \right) - \sum_i^{electrons} \sum_s^{nuclei} \left(\frac{Z_s}{r'_{is}} \right) + \sum_{i < j}^{electrons} \left(\frac{1}{r'_{ij}} \right) + \sum_{s < t}^{nuclei} \left(\frac{Z_s Z_t}{R'_{st}} \right) \quad (2.1.14)$$

Energies are given in terms of the hartree which has a value of approximately 27.21 eV or 2626 kJ mol⁻¹. The bohr has a value of 0.529117×10^{-10} m and is equivalent to the radius of the 1s orbit in the Bohr model for the hydrogen atom.

2.2 Variation theorem and the self consistent field(SCF) method

2.2.1 Introduction

The repulsion between the electrons makes it difficult to separate the n-electron Schrödinger equation into a set of one-electron equations. Therefore, correct solutions of the electronic Schrödinger equation are very hard to obtain for atoms and molecules. Electronic wavefunctions are obtained under the assumption that the nuclei are fixed. For atoms a single nucleus exists and only the positions of the electrons relative to the nucleus are taken into account. The one-electron wavefunctions for atoms in terms of their positions are defined as atomic orbitals.

In the similar way, the one-electron wavefunctions for molecules are termed molecular orbitals. For the hydrogen atom or the H_2^+ molecule, exact solutions of the electronic Schrödinger equation can be obtained directly whereas for many electron atoms or molecules approximate methods have to be used. Recently it has been shown that Monte Carlo methods can be applied to the electronic Schrödinger equation and have been able to provide accurate results for many-electron systems. For the molecule the wavefunction consists of an antisymmetrized product of molecular orbitals. Each individual electron is in an orbital. This antisymmetrized product can be expressed as a Slater determinant. Furthermore, each of the one-electron orbitals can be represented as a complicated linear combination for atomic orbitals. Molecular electronic structure can be expressed in terms of the molecular orbital method. Even if this method does not give the accurate information for molecular dissociative processes it can give good results for molecular properties close to their equilibrium configurations. In addition, the molecular-orbital wavefunction for a molecule is

usually is taken as the starting point for a more accurate calculation. The molecular orbital method is based on an independent particle model for the molecular electronic wavefunction. If the electron-electron repulsion is ignored the electronic Schrödinger equation for n electrons can be separated into n one-electron Schrödinger equations and the wavefunction written as a product of one electron functions. The Hartree-Fock method takes a wavefunction in the form of an antisymmetrized product of one electron functions and the Hartree-Fock equations are derived from the condition that the expectation value of the energy, E , has to be minimized. The Hartree-Fock equations are integro-differential equations which can only be solved by an iterative method. This procedure is carried on until convergence has been reached. This method is named the self consistent field (SCF) method. Although the wavefunction is of the independent particle type, the Hartree-Fock method does include electron-electron repulsion in the Hamiltonian.

2.2.2 The variation method

The Hartree-Fock method has an important relationship with the variational method in quantum mechanics [142]. If Φ is defined as any antisymmetric normalized function of the electronic coordinates, then the expectation value of the energy corresponding to this function is given by the integral

$$E' = \int \Phi^* \hat{H}^{elec} \Phi d\tau . \quad (2.2.1)$$

Here, integration is over the coordinates of all electrons and the asterisk represents the complex conjugate. If Φ is identified as the exact wavefunction, Ψ , for the electronic ground state, the Schrödinger equation (2.1) will be solved. Because Ψ is normalized,

E' will be the exact ground state energy E as shown below,

$$E' = E \int \Psi^* \Psi d\tau = E . \quad (2.2.2)$$

However, if Φ is any other normalized antisymmetric function, it can be shown that E' is greater than E as follows,

$$E' = \int \Phi^* \hat{H}^{elec} \Phi d\tau > E. \quad (2.2.3)$$

It follows that if Φ is the antisymmetric molecular orbital function (2.2.7) which will be described in the following section 2.3, the energy E' obtained from (2.2.1) above will be higher than the exact ground state energy E .

To optimize the orbitals in a single determinantal wavefunction, the orbitals are expanded in terms of a basis set and the coefficients c_{is} from equation (2.2.16), which will be mentioned in the section 2.2.3 may be varied to minimize the expectation value E' . The minimized value of E' will be as close the exact energy E as is possible with a single - determinant wavefunction and the chosen basis set. Therefore, the best single determinant wavefunction has been obtained by minimizing E' with respect to the coefficients c_{is} . This leads to the variational equations expressed as follows

$$\frac{\partial E'}{\partial c_{is}} = 0 \quad (\text{all } i,s) \quad (2.2.4)$$

2.2.3 Theory of the self consistent field method

The molecular-orbital method makes use of a form of wavefunction suitable for the independent particle model. If the interelectronic repulsion is ignored in equation (2.1.5) for an n-electron Schrödinger equation, the Schrödinger equation (2.1.5) for n-electrons can be separated into n one-electron Schrödinger equation which can be solved to produce a set of n one-electron functions $\phi_i(r)$, where $i = 1, 2, \dots, n$.

Thus, the total electronic wavefunction is described as a product of n one-electron functions given below.

$$\Phi(R, r) = \phi_1(r_1)\phi_2(r_2)\dots\phi_n(r_n). \quad (2.2.5)$$

Each one-electron function $\phi_i(r_i)$ can be written down as the product of a spatial function $\psi_i(r_i)$ and a spin function α or β which is dependent on the spin's direction (up or down). Each spatial orbital can be occupied by up to two electrons, one with α -spin and one with β -spin. If each spatial orbital is doubly occupied and the number, n , of the electrons is even, the total electronic wavefunction $\Phi = (R, r)$ is given as follows.

$$\Phi(R, r) = \psi_1(r_1)\alpha\psi_1(r_2)\beta\psi_2(r_3)\alpha\dots\psi_{n/2}(r_{n-1})\alpha\psi_{n/2}(r_n)\beta \quad (2.2.6)$$

By using two conditions which are to take into account the indistinguishability of the electrons and to make certain that the wavefunction satisfies the Pauli principle, the wavefunction can be expressed as a Slater determinant as follows.

$$\Phi(R, r) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(r_1)\alpha & \psi_1(r_1)\beta & \dots & \psi_{n/2}(r_1)\beta \\ \psi_1(r_2)\alpha & \psi_1(r_2)\beta & \dots & \psi_{n/2}(r_2)\beta \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_n)\alpha & \psi_1(r_n)\beta & \dots & \psi_{n/2}(r_n)\beta \end{vmatrix} \quad (2.2.7)$$

Interchange of two electrons leads to interchanging the labels for the electronic coordinate. This causes a change of sign in accordance with the Pauli principle. The Slater determinant above can be written in the shortened form below.

$$\Phi = |\psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\dots\psi_{n/2}\alpha\psi_{n/2}\beta| \quad (2.2.8)$$

In order to minimize the energy for the wavefunction $\Phi(R, r)$ the orbitals ψ_i are derived using the variation method. The energy is given by the expectation value, E , of the electronic Hamiltonian, H^{elec} , and is represented as the integral

$$E_{approx} = \frac{\int \Phi(R, r)^* H^{elec}(R, r) \Phi(R, r) d\tau}{\int \Phi(R, r)^* \Phi(R, r) d\tau} \quad (2.2.9)$$

As described earlier in the section 2.1, the electronic Hamiltonian is shown as follows

$$H^{elec}(R, r) = T^{elec} + V \quad (2.2.10)$$

The integration is over the whole of space and $d\tau$ describes a suitable volume element.

The requirement that the expectation value, E , generated from (2.2.9) has to be minimized leads to the Hartree-Fock equations

$$\hat{F}_i(1)\psi_i(1) = \varepsilon_i\psi_i(1), \quad (2.2.11)$$

where ε_i is the orbital energy for orbital i and \hat{F}_i is the Fock operator which is given by

$$\hat{F}_i(1) = \hat{h}(1) + \sum_j [2\hat{J}_j - \hat{K}_j(1)]. \quad (2.2.12)$$

Here $\hat{h}(1)$ represents a one-electron operator given by

$$\hat{h}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\alpha=1}^N \frac{Z_\alpha}{r_{1\alpha}}. \quad (2.2.13)$$

The Coulomb and exchange operators \hat{J}_j and \hat{K}_j are expressed in terms of the coulomb and exchange integrals by the relationships

$$J_{ij} = \int \psi_i(1)J_j(1)\psi_i(1)d\tau_1 = \int \psi_i(1)\psi_j(2)\frac{1}{r_{12}}\psi_i(1)\psi_j(2)d\tau_{12} \quad (2.2.14) \text{ and}$$

$$K_{ij} = \int \psi_i(1)K_j(1)\psi_i(1)d\tau_1 = \int \psi_i(1)\psi_j(2)\frac{1}{r_{12}}\psi_i(2)\psi_j(1)d\tau_{12}. \quad (2.2.15)$$

The Hartree-Fock equations have to be solved iteratively because the \hat{J}_j and \hat{K}_j operators in \hat{F}_i are dependent on the orbitals ψ_i . The Hartree-Fock equations are a set of coupled integro-differential equations which can be solved by an iterative

method. Typical iterative methods start with an initial guess for orbitals ψ_i , from which the operators \hat{F}_i are calculated. Solution of the Hartree-Fock equations (2.2.11) provides a new set of orbitals ψ_i , which should be an improvement on the initial set. The new orbitals ψ_i , which possess the correct symmetry, suitable energies and nodal character are used to derive a new Fock operator \hat{F}_i from the new \hat{J}_i and \hat{K}_i operators. By the same method, the new set of equations produces a third set of orbitals ψ_i . This iterative process is continued until convergence based on the energy and the orbitals is reached. Thus, this iterative procedure is named the self-consistent field (SCF) method. It is possible to calculate the Hartree-Fock equations numerically for atoms which contain spherical symmetry to obtain the atomic orbitals whereas this is not easily carried out for molecules which have lower symmetry. This obstacle can be removed by the method adopted by Hall [143] and Roothaan [144] where the orbitals ψ_i are expressed as linear combinations of a set of basis functions $\{x_s\}$ as follows

$$\psi_i = \sum_s c_{is} x_s. \quad (2.2.16)$$

The expansion coefficients c_{is} are obtained by using an iterative method and the set of functions $\{x_s\}$ is termed the basis set which will be discussed in the following section 2.3.

Up to now much of the description has been given for closed shell systems where doubly occupied orbitals are allowed for which the SCF wavefunction can be expressed as a single Slater determinant as in equation (2.2.7).

For open shell systems, every orbital does not need to be doubly filled. Open shell systems are described by two theories which are the restricted Hartree-Fock (RHF) method and the unrestricted Hartree-Fock (UHF) method. In the case of the RHF method, a single set of molecular orbitals is used for the closed shell part of the wavefunction and the open shell orbitals are singly occupied with electrons of α spin. As described earlier in the RHF method, the molecular orbital wavefunction does not generally provide an accurate description of potential energy surfaces. Also, the molecular orbital wavefunction does not usually dissociate correctly because for a closed shell molecule it is expressed in terms of a set of doubly occupied molecular orbitals

$$\Phi = |\psi_1 \alpha \psi_1 \beta \psi_2 \alpha \psi_2 \beta \dots \psi_{n/2} \alpha \psi_{n/2} \beta|. \quad (2.2.17)$$

This obstacle can be eliminated in the UHF method by using different spatial orbitals for α and β electrons with the constraint of doubly occupied orbitals being loosened. Thus, the pair of electrons $\psi_i \alpha \psi_i \beta$ is represented in terms of two separate orbitals ψ_{ia} and ψ_{ib} with singlet coupled electron spins

$$\Phi = |\psi_1 \alpha \psi_1 \beta \dots \psi_{ia} \psi_{ib} (\alpha \beta - \beta \alpha) \dots \psi_{n/2} \alpha \psi_{n/2} \beta| \quad (2.2.18)$$

Since the RHF function can be expressed as a specific case of the UHF functions, from the variational method it can be shown that the optimized UHF energy should be lower than the optimized RHF energy. However, UHF functions have the disadvantage that they are not eigenfunctions of the total spin operator S^2 . If the expectation value of the total spin angular momentum does not differ very much from the true value, the UHF method leads to a reasonable molecular wavefunction.

2.3 Basis functions

2.3.1 Introduction

In an ab initio calculation, a particular basis set is chosen for the calculation of the electronic wavefunction. In some cases a reasonable choice of basis set yields correct results which can be comparable to experimental parameters, whereas the wrong choice of basis set gives results which are in disagreement with experimental data. Therefore, accurate potential energy surfaces can only be obtained with the appropriate choice of basis set. That is, choice of a suitable set of basis functions leads to the success of an ab initio calculation. It is necessary that a reasonably small basis set should be chosen but the basis set chosen must not be so small that the accuracy of the results is adversely affected. In the previous section, it is shown how a many-electron wavefunction is formed from molecular orbitals with a single determinant.

The individual molecular orbitals have been expressed as linear combinations of a set of one-electron functions called basis functions. If the basis functions are x_1, x_2, \dots, x_n , then an individual orbital ψ_i can be expressed as shown previously

$\psi_i = \sum_s c_{is} x_s$ where c_{is} are the molecular orbital expansion coefficients. In molecular

orbitals, atomic orbitals are used as basis functions. This procedure is usually called the linear combination of atomic orbital (LCAO) approximation. For a well defined basis set for a nuclear configuration and to produce a useful theoretical model, it is very reasonable to select a particular set of basis functions on each nucleus, which depend on the charge on that nucleus. Such functions should have the symmetry properties of atomic orbitals and are termed s, p, d, f, ... types depending on their

angular characteristics. In general, there are two types of commonly used atomic basis sets namely Slater-type atomic orbitals (STOs) and gaussian-type atomic functions. However, using these two general functions several kinds of basis functions can be devised which are, for example, STO-nG basis sets, split-valence basis sets and even-tempered basis sets and so forth.

2.3.2 Polarization functions

Even if a suitable set of the basis functions χ has been chosen, such a calculation would be limited in accuracy and would produce a wavefunction and energy quite different from the Hartree-Fock limit. Thus, to double the number of functions chosen should give a significant improvement in accuracy. In the case of methane, for instance, a minimal basis set consists of 1s, 2s, and 2p functions on the carbon atoms and 1s functions on each of the hydrogen atoms. An improved description is given by choosing two 1s functions, two 2s functions and two sets of 2p functions for carbon and two 1s functions for each hydrogen atom. In general, such a basis set is called a double-zeta (DZ) basis. So far it has been assumed that the molecular orbitals are composed of atomic functions for the atoms considered. However, such a basis set does not describe an important phenomenon which occurs during bond formation namely distortion by one atom of the atomic orbitals on neighboring atoms. This difficulty can be solved by including orbitals with higher values of the l quantum number. Therefore, the distortion of the 1s orbital on the hydrogen atom can be accounted for including p-functions and for the heavier atoms the distortion of p orbitals can be described by including d functions. Such functions are named

polarization functions. Addition of a set of p functions for each hydrogen atom and a set of d functions for heavier atoms to a double-zeta (DZ) basis set gives a double-zeta plus polarization (DZP) basis set. Such a basis set can give a reasonable description of a molecule for the ground or low-lying excited states.

2.3.3 Diffuse functions

To obtain the Hartree-Fock limit one needs much larger basis sets. If highly excited states are taken into account, the excitation may be to a diffuse Rydberg orbital.

To give an adequate description of such states suitable diffuse functions for higher principal quantum number should be included in the basis set.

If diffuse Rydberg functions are not considered the calculation will not be meaningful.

For the negative ion calculations it is necessary to expand the standard basis sets for valence orbitals by including additional diffuse functions to obtain the description of the more diffuse orbitals of the negative ion.

2.3.4 Slater-type functions

The solution of the Schrödinger equation for hydrogen-like atoms suggests the use of atomic orbitals of the form

$$x_{nlm} = r^{n-1} \exp(-\mathcal{G}) Y_{lm}(\theta, \phi). \quad (2.3.1)$$

The radial function consists of a power of r multiplied by an exponential function.

Generally this kind of function can be normalized by multiplying by a suitable constant and is named a Slater-type orbital (STO) expressed as follows

$$x_{nlm} = N_{nlm} r^{n-1} \exp(-\zeta r) Y_{lm}(\theta, \phi). \quad (2.3.2)$$

where n , l and m are the usual atomic quantum numbers, N_{nlm} is a normalization factor and $Y_{lm}(\theta, \phi)$ is a spherical harmonic. The coordinates r , θ and ϕ represent the position of the electron relative to the centre of the basis orbital. To tabulate reasonable values of minimal, DZ, DZP basis sets is useful [155] but there is a major problem for Salter-type functions namely that it is very difficult to compute accurately two-electron integrals in which the four functions are situated on three or four different atomic centres. Thus, the integral calculation is very time consuming. Even though Slater-type orbitals (STOs) possess the required cusp at the nuclei, they can not be widely used in molecular calculations because the multicenter integrals that occur for polyatomic-molecule calculations can not be efficiently calculated using Slater-type orbitals (STOs).

2.3.5 Gaussian-type functions

If the exponential functions given in equation (2.3.2) are utilized, it is very difficult to calculate the required molecular integrals. Thus, most molecular calculations are preformed with Gaussian basis sets. These are of the form of a power of x , y , z multiplied by $\exp(-\alpha r^2)$ where α is a constant which determines the radial size of the basis function. Thus, Gaussian functions are written down as follows

$$x_{a,b,c}(r, \theta, \phi) = N'_{a,b,c,\alpha} x^a y^b z^c \exp(-\alpha r^2) \quad (2.3.3)$$

The quantum numbers a , b and c account for the angular shape and direction of the orbital. Compared to STOs, the advantage for Gaussian functions is that for a two-electron integral the product of two orbitals on different centres can be represented as

a single Gaussian function at a centre located on a line joining the two centres. Thus, the calculation of the required integrals is much quicker with Gaussian-type orbitals (GTOs). This advantage of GTOs is the reason for the computational superiority of these functions. However, the major disadvantage of the Gaussian function is that Gaussian basis sets provide a less reasonable description of atomic wavefunctions because a Gaussian function is not close to the form of a real atomic orbital wavefunction. There is, for example, a cusp in an exponential 1s function at the nucleus for a Slater function whereas there is no cusp in a Gaussian function. If the orbital exponent is fixed and the functions are identified reasonably close in the intermediate region, the Gaussian function will show important deviations in the long-range region. Therefore, to obtain accuracy comparable to that obtained using Slater-type exponential functions a large number of Gaussian basis functions should be used. In other words, to overcome the major difficulty of GTO functions it is necessary to take two, three or more GTOs in linear combinations. In the SCF calculation the contraction coefficients are unchanged and not varied as LCAO-MO parameters. These new functions are named contracted GTOs or CGTOs. Usually, a series of GTOs with large, medium, small sized orbital exponents are multiplied by contraction coefficients and summed to obtain a CGTO which gives a reasonable description of the cusp at the nuclear centre.

2.3.6 STO-nG basis sets

This basis set is one of the contracted Gaussian basis functions mentioned above. Slater functions are expanded in terms of a linear combination of n Gaussian functions.

The expansion coefficients and exponents are determined to provide the best fit to the Slater orbital. The basis set obtained from the expansion of a Slater function in terms of n Gaussian function is called a STO- n G basis. Even though this expansion could be used for all of the orbitals in a DZ, DZP basis set, the use of STO- n G basis sets is generally limited to calculations with minimal basis sets.

2.3.7 Split-valence basis sets

The split-valence basis set is a different type of contracted Gaussian basis set adopted by Pople and his coworkers. For instance, a 6-31G basis set for first-row atoms is composed of an s- type inner shell function, a set of valence s- and p- type functions and an outer set of s- and p- functions. An s- type inner shell function is expressed as a combination of six Gaussian functions. A set of valence s- and p- type functions is each written as a combination of three Gaussian functions. An outer set of s- and p- functions each consist of a single Gaussian function. A 6-31G basis expanded with d-polarization functions for the heavy atom is named 6-31G*. On the other hand, the addition of the p-functions on hydrogen atoms to the 6-31G* basis is called a 6-31G** basis.

2.3.8 Even-tempered basis set

To obtain high accuracy for molecular calculations it is reasonable to add extra basis functions to the basis set rather than to try to optimize exhaustively the orbital exponents. Thus, even-tempered basis set which contains a limited number of

parameters can be used. Each basis function is represented as the product of a spherical harmonic $Y_{lm}(\theta, \phi)$ and a function $r^l \exp(-\zeta_k r^2)$. Therefore, the basis set is composed of 1s, 2p, 3d, 4f, . . . functions as follows

$$x_{klm}(r, \theta, \phi) = \exp(-\zeta_k^2) r^l Y_{lm}(\theta, \phi) \quad (2.3.4)$$

The orbital exponents, ζ_k are accounted for in terms of two parameters, α and β , by a geometrical sequence

$$\zeta_k = \alpha \beta^k \quad (k = 1, 2, \dots, N) \quad (2.3.5)$$

for a particular set of GTOs. For each group of functions of the same symmetry species only two parameters, α and β have to be optimized. Therefore, large basis sets can be obtained effectively.

2.4 Electron correlation

The wavefunction produced from the Hartree-Fock method is based on the independent particle method which does not account fully for the interelectronic repulsion between electrons of opposite spin. Thus, even if the SCF method considers interelectronic repulsion by characterizing Coulomb and exchange operators \hat{J} and \hat{K} with the effective field due to other electrons, a single determinantal wavefunction in equation (2.2.7) for a closed shell molecule cannot represent the true wavefunction.

Because of the limitation of the wavefunction to doubly occupied molecular orbitals the interelectronic repulsion is not completely described. The difference between the energy of the Hartree-Fock wavefunction and the exact non-relativistic energy is named the correlation energy. Because the correlation energy will generally be different from one part of the surface to another, the theoretical surface will not be parallel to the exact surface at all points. Therefore, to produce realistic potential surfaces electron correlation should be considered. At the same time this will generally ensure the correct dissociation of the wavefunction. In general electron correlation is composed of two components, namely dynamical and non-dynamical correlation.

The dynamical correlation is concerned with the correlation between the motion of the electrons derived from the Coulomb interaction between the electrons. This effect is omitted in the SCF method in which interelectronic repulsions are effectively averaged.

Non-dynamical correlation is about other deficiencies of the wavefunction such as the difficulty of accounting for dissociation or correct degeneracies. Non-dynamical correlation effects can be generally accounted for by a relatively restricted CI.

For the calculations described in this thesis both sorts of electron correlation have been taken into account by using the multi-configuration SCF (MCSCF) and configuration interaction (CI) methods

2.4.1 Multi-configuration SCF method

2.4.1.1 Introduction

There are many methods used currently to produce the best wavefunction of the form

$$\Phi = \sum_I C_I \Phi_I \quad (2.4.1)$$

In all such wavefunctions, there are two different sorts of parameters namely the CI coefficients C_I and the molecular-orbital expansion coefficients c_{iq} .

The simultaneous optimization of both sets of coefficients is required to obtain an improved molecular wavefunction. The MCSCF method is much more difficult than the conventional SCF method because the two parameters mentioned above should be optimized at the same time. Initially it was only possible to treat a small number of configurations in the expansion due to computational obstacles.

However, these difficulties have now been overcome and it is now possible to include more configurations and to obtain the best wavefunction with the complete active space SCF (CASSCF) method.

2.4.1.2 Theory

In the CASSCF method the orbitals are divided into three categories, namely inactive orbitals, active orbitals and virtual orbitals. First, the lowest orbitals, which are defined as the inactive orbitals, are doubly occupied in all configurations.

Second, the highest orbitals, which are named the virtual orbitals, are unoccupied in all configurations. Finally the active orbitals are set in between the inactive orbitals and virtual orbitals. In the CASSCF method the configuration list is composed of those configurations of suitable symmetry and spin produced from all permutations of the active electrons among the active orbitals. Thus, for a chosen set of active orbitals it is impossible to ignore an important configuration involving the active orbitals. Once the set of active orbitals has been chosen, the configuration list is defined.

For small molecules the active space would involve at least the valence-bonding and antibonding orbitals. A CASSCF calculation which has no unoccupied valence orbitals of the same symmetry as one of the occupied orbitals would be unbalanced because no orbital is correlated with the occupied orbitals. It is very important to choose the set of active orbitals carefully because the number of configurations will rise very drastically with the size of the active space.

2.4.2 Configuration interaction

2.4.2.1 Introduction

The single determinant molecular orbital wavefunction does not generally give a reasonable description of potential energy surfaces and even if the wavefunction dissociates correctly the molecular orbital method will not have comparable accuracy at all points on the surface because electron correlation is neglected. These difficulties can be solved by the method of configuration interaction. The configuration interaction method starts with an appropriate set of molecular orbitals which are expressed as linear combinations of a set of atomic basis functions.

2.4.2.2 Theory

If Φ_0 is the SCF-MO wavefunction for an n -electron system where $n/2$ orbitals are doubly occupied, the SCF-MO calculation with a basis set of m functions provides a further $m - n/2$ virtual orbitals. By exciting electrons from the occupied orbitals to the virtual orbitals further determinantal functions can be generated. These will not generally have the same spin and symmetry as Φ_0 but, where necessary, linear combinations can be generated with the required spin and symmetry. If the set of all such configuration state functions (CSF) is $\{\Phi_i\}, i = 1, \dots, N$, the configuration interaction method applies the variation method to a linear combination of the CSF's $\Phi_i, i = 1, \dots, N$,

$$\Phi = \sum_{i=0}^N c_i \Phi_i \quad (2.4.2)$$

The lowest root from the secular determinant will give the best wavefunction for the ground state with the basis set chosen. No other wavefunction with the same basis set will lead to a lower variational energy. Higher roots generated also represent upper bounds to the exact energies for excited states with the same spin and symmetry.

Electron correlation is accounted for and the wavefunction dissociates correctly because although Φ_0 may not correspond to the dissociation fragments, the CI wavefunction will involve configurations corresponding to those fragments. However, CI cannot correct for deficiencies in the basis set and accurate results will only be obtained if a realistic basis set is used. In most cases the number of configurations arising from all possible excitations from Φ_0 is too large to treat. Thus, some limitation is required on the excitations considered. In restricting the number of configurations all parts of the surface should be treated with comparable

accuracy. If several surfaces are considered they have to be described on a comparable basis and to have correct asymptotic dissociation in all cases. If two CSF's, Φ_i and Φ_j , differ by more than two orbital occupancies, it can be shown that the integral $\int \Phi_i H \Phi_j d\tau$ is zero. Thus, no direct interaction will be allowed between Φ_0 and configurations for which more than two electrons have been excited from the orbitals occupied in Φ_0 to virtual orbitals.

In the closed-shell case, according to Brillouin's theorem, for a single excitation Φ_i , the integral $\int \Phi_0 H \Phi_i d\tau$ is zero if Φ_0 represents the SCF-MO wavefunction for the ground state. Thus, in the closed-shell case there will not be an interaction between Φ_0 and single excitations and the single excitations will have a negligible effect on the energy. However, single excitations can play an important role in the calculation of molecular properties for closed-shell molecules.

For open-shell molecules single excitations are very significant and should be contained in the configuration list. Analysis of the closed-shell case by perturbation theory shows that the first-order correction to the wavefunction is obtained from the double excitations. In CI methods it is sometimes necessary to include single excitations to obtain a dipole moment having the correct sign [145]. Thus, a reasonable initial approximation of the configuration list is limited to single and double excitations from Φ_0 . However, to obtain a reasonable description of several surfaces and to account for correct dissociation single and double excitations should also be chosen with respect to those configurations which correspond to the excited states and those which are needed to describe accurately the dissociation asymptotes. For accurate work the calculation should consider such excitations produced from all configurations which

include a coefficient c_i greater than 0.1 in the final CI wavefunction. In general this involves making several preliminary calculations to find which configurations have to be included in the set of multiple reference configurations $\{\Phi_k\}$ from which single and double excitations are generated. Except for the smallest of molecules this will still lead to a prohibitively large number of configurations. Some saving can be made if the inner shell orbitals are kept doubly occupied and with the exclusion of excitations to the corresponding high energy virtual orbitals. This will usually not result in any loss of accuracy. To reduce the length of the configuration lists further limitations may be imposed on the excitations considered. However, to include all important excitations it is reasonable not to limit too drastically all the single and double excitations considered. An alternative treatment to reduce the configuration lists is to use an efficient internally contracted method of Knowles and Werner[150,151], which is a way of generating configurations from a reference set but resulting in about 10 % of full configuration list. Another approach is to determine the important configurations by calculating a zero-order CI wavefunction from the set of reference configurations $\{\Phi_k\}$ and then evaluating by perturbation theory the energy lowering obtained from including a certain configuration. All configurations generated from $\{\Phi_k\}$ are examined by this method. Those configurations which lead to a lowering of the calculated energy by less than a certain threshold energy between $10^{-4} E_h$ and $10^{-5} E_h$ ($1E_h = 4.359814 \times 10^{-18} \text{ J}$) are discarded. The calculation of the wavefunction is then carried out with the set of chosen configurations.

2.5 Effective core potentials

2.5.1 Introduction

The *ab initio* calculations discussed previously include all the electrons in the molecule. The size of the calculation rises drastically as the number of basis functions increases. The number of two-electron integrals, for instance, which should be produced and manipulated is approximately proportional to the fourth power of the size of the basis set. Thus, for good quality *ab initio* CI calculations it is only reasonable to consider relatively small molecules involving light atoms with a suitable basis set. However, the electrons of a molecule may be divided into two groups, namely the core electrons, which occupy the inner shell orbitals, and the valence electrons. The valence electrons are fundamentally responsible for chemical bonding and electrons from inner shells have little influence on the bonding. Instinctively it should be possible to invent methods which only take into account the valence electrons with the core electrons kept fixed and thus simply reduce the size of calculations for heavier atoms. With the help of some approximations it is possible to make the computational effort smaller for a CI calculation by keeping the core orbitals frozen.

2.5.2 Theory

The total electronic wavefunction is expressed as follows

$$\psi = A(\psi_{core} \psi_{valence}) \quad (2.5.1)$$

where A accounts for the antisymmetrizer, ψ_{core} and $\psi_{valence}$ represent wavefunctions for the core and valence electrons respectively. If $\psi_{valence}$ is orthogonal to ψ_{core} , the total energy can be represented as

$$E_{total} = E_{core} + \int \psi_{valence} H_v \psi_{valence} d\tau \quad (2.5.2)$$

H_v is expressed as the valence Hamiltonian of the form

$$H_v = \sum_v (h_v + \sum_c g_{vc}) + \sum_{v,v'} \frac{1}{r_{vv'}} \quad (2.5.3)$$

where h_v is the one-electron energy of the valence electron v , g_{vc} describes an operator showing the effect of core electron c on valence electron v and the term $1/r_{vv'}$ accounts for the interelectronic repulsion between valence electrons v and v' .

For the evaluation of the terms g_{vc} the two-electron integrals are required with respect to both core and valence electrons and so no saving is made at the SCF level. However, important savings in computational effort can be achieved in CI calculations if the inner shell orbitals are kept doubly occupied. If an approximate valence Hamiltonian is written in the form

$$H_v \approx \sum_v [h_v + U^{core}(v)] + \sum_{v>v'} \frac{1}{r_{vv'}} \quad (2.5.4)$$

where $U^{core}(v)$ represents an effective core potential expressing the effect of the core electrons on the valence electrons, then calculations can be carried out which only take into account the valence electrons. The simplest method is to use an effective core potential with an appropriate functional form, or model potential, which may simply be a radial function or may be angle dependent.

3 Computational Procedure

3.1 MOLPRO system

MOLPRO is a suite of *ab initio* programs for carrying out molecular electronic structure calculations developed by H. -J. Werner and P. J. Knowles.

Unlike other frequently used quantum chemistry package, MOLPRO is focused on highly accurate calculations for small molecules with an extensive treatment for electron correlation by multiconfiguration-reference CI wavefunctions. In this program the major parts are concerned with the multi-configuration SCF (MCSCF) and multi-reference CI (MRCI). The multi-configuration SCF program in the MOLPRO system uses the quadratically convergent MCSCF procedure [146]. This program can optimize a weighted energy average for several states and handle both perfectly general configuration expansions and long CASSCF expansions [147]. The MRCI program in this system uses the internally contracted multi-reference CI method [150,151].

In this work we have carried out theoretical calculations on NF^+ , PCl^+ , BBr^+ and AsCl^+ for diatomic molecules and $\text{HC} + \text{NO}$ with the MOLPRO system. This work comprises three stages, namely an SCF calculation, a MCSCF(CASSCF) calculation and a CI calculation.

3.2 SCF calculation

The Hartree-Fock self-consistent field calculation has been performed by using one of the three directives, namely HF, RHF and UHF.

HF which represents HF-SCF defines the closed-shell SCF calculation.

RHF represents RHF-SCF and specifies the spin-restricted open shell Hartree-Fock calculation. UHF(UHF-SCF) represents the spin-unrestricted open-shell

Hartree-Fock calculation. For our work the RHF-SCF method has been chosen to generate a starting set of molecular orbitals.

Generally no further input is required. However, usually it is recommended to include the WF card which defines the number of electrons and the symmetry of the wavefunction. Also, the OCC card is required to characterize the wavefunction and to eliminate convergence problems because of alternation between different occupied orbital spaces. If the WF card is absent, the number of electrons is equivalent to the nuclear charge and it is assumed that the wavefunction is generally symmetric (symmetry 1). By default, the spin multiplicity is taken to be 1 (singlet) for an even number of electrons and 2 (doublet) otherwise. If the OCC card is omitted, the Aufbau principle is utilized to decide the occupation numbers.

3.2.1 The wavefunction

To define the wavefunction, as mentioned above, the number of electrons and total symmetry of the wavefunction are needed.

The wavefunction is specified in the form

WF,elec,sym,spin

where *elec* is the number of electrons and *sym* represents the number of the irreducible representation, *spin* specifies the spin symmetry, $spin = 2 * S$ (singlet = 0, doublet = 1, triplet = 2 and so on). Only even numbers of electrons and singlets can be treated by

the HF-SCF method and only high-spin cases (one Slater determinant) by the RHF-SCF method.

3.2.2 Occupied orbitals

The number of occupied orbitals is defined as follows

OCC, n_1, n_2, \dots, n_8

To minimize convergence problems, this card should be used whenever the occupation pattern is identified in advance. n_i describes the number of occupied orbitals in the irreducible representation i . The total number of orbitals should be the same as $(elec + spin) / 2$.

3.2.3 Closed-shell orbitals

The directive for the closed-shell orbitals is given by

CLOSED, n_1, n_2, \dots, n_8

This optional card can be useful for RHF calculations to define the number of the closed-shell orbitals in each symmetry. This makes it possible to force convergence to specific states without an OPEN card.

3.2.4 Open-shell orbitals

The open-shell orbital command is represented as follows

OPEN, $orb_1.sym_1, orb_2.sym_2, \dots, orb_n.sym_n$

This optional card can be used to characterize the singly occupied orbitals. The number of singly occupied orbitals should be equivalent to the spin and their symmetry

product has to correspond to *sym*. If the OPEN card is missing, the open shell orbitals are determined automatically.

3.2.5 Starting orbital guess

The initial orbitals are specified with

START, *orb.file*, *neig.neigf*

The starting orbitals are obtained from the record *orb.file*. The orbital occupancy can be defined by WF, OCC, [CLOSE, OPEN] cards. If this is not done, the Aufbau principle is adopted with orbital energies generated from *neig.neigf*. By default, *neig* = *orb* + 100 and *neigf* = *file*. If these orbital energies are not found, the eigenvalues of *h* are utilized. If the START card is not present, the program will find suitable starting orbitals by the following three methods.

First, the program attempts to read orbitals from the record defined on the ORBITAL or SAVE card or the corresponding default. All files are searched.

Second, the program tries to search for orbitals from a previous SCF calculation. All files are searched. Third, if no orbitals are found, the eigenvectors of *h* are used. This can be forced by setting *orb.file* to zero. Because these defaults are generally suitable, the START card is not always needed.

3.2.6 Saving the final orbitals

The directive is of the form

ORBITAL, *record.file*

or SAVE, *record.file*

The optimized orbitals are saved on *record.file* and the Hartree-Fock orbital eigenvalues are saved on *record + 100.file*. SAVE is an alias for ORBITAL. If this is missing, the defaults are record 2100 for HF-SCF, 2110(α -spin orbitals) and 2120(β -spin orbitals) for UHF-SCF and 2130 for RHF-SCF. These numbers are increased by one for each following calculation of the same type in the same job. The counter is reset for each new geometry. The default for *file* is 2.

3.3 MCSCF calculation

The MCSCF calculations have been performed by the program MULTI which uses the MCSCF/CASSCF method devised by P.J. Knowles and H. -J. Werner(1984). This program [146-149] (From USER's MANUAL FOR MOLPRO 94) enables one to carry out both CASSCF and general MCSCF calculations. For CASSCF calculations Slater determinants or CSFs can optionally be used as the N-electron basis.

In most cases it is more effective to use Slater determinants. For general MCSCF calculations CSF's should be used as a basis. A well defined optimization method has been chosen. The algorithm is second-order for changes in the orbital and CI coefficients and thus is quadratically converged. Because significant higher order terms are contained in the independent orbital parameters, cubic convergence is usually often obtained. For simple cases, convergence is generally obtained within 2-3 iterations. However, convergence problems can arise in certain applications, and generally indicate that the active space has not been suitably selected.

In such cases, this problem can be overcome by either reduction or enlargement of the active orbital space. In other cases problems can arise if two electronic states are

nearly or precisely degenerate, since then the program is able to exchange from one state to the other. This difficulty might occur near avoided crossings or near an asymptote. This kind of problem can be eliminated with the optimization of the energy average of the specific states. It is also possible to force convergence to particular states by selecting a subset of configurations as primary space(PSPACE). The hamiltonian has been clearly chosen and diagonalized in this space; the coefficients of the remaining configurations are converged repeatedly with the P-space wavefunction as zeroth order approximation. For linear molecules, another approach is to utilize the LQUANT option which makes it possible to force convergence to states with definite Λ quantum numbers, that is, Σ , Π , Δ states and so on.

3.3.1 Occupied orbitals

These are specified with OCC, n_1, n_2, \dots, n_8 ;

n_i defines numbers of occupied orbitals (including CORE and CLOSED) in irreducible representation number i . If an OCC card is not present, the information obtained from the most recent MCSCF calculation is used. If the information is not available, those orbitals are used which are equivalent to a minimal valence set, that is, full valence space.

3.3.2 Frozen-core orbitals

The command is defined of the form

CORE, $n_1, n_2, \dots, record.file$;

n_i accounts for the number of frozen-core orbitals in irreducible representation

number i . These orbitals are doubly occupied in all configurations and not optimized. *record.file* represents the record name for frozen core orbitals; if not presented, they are obtained from *orb* on the START card. *record.file* can be characterized in any field after the last nonzero n_i . It should generally be provided if the orbital guess is generated from a neighbouring geometry and then has to define the SCF orbitals to be computed at the present geometry. If a subsequent gradient calculation is carried out with this wavefunction, *record.file* is compulsory and should characterize closed-shell scf orbitals at the present geometry. It is necessary that *record* is bigger than 2000. In the absence of the CORE card, the numbers of core orbitals are given from the most recent MCSCF calculations, or otherwise no orbitals are frozen. If the CORE card is given as CORE, *record.file*, then the orbitals which correspond to atomic inner shells are chosen. A CORE card without any specification resets the number of frozen core orbitals to zero.

3.3.3 Closed-shell orbitals

The orbital directive is of the form

CLOSED, n_1, n_2, \dots, n_8

n_i expresses the number of closed-shell orbitals in irreducible representation number i , including any CORE orbitals. These orbitals are not part of the active space, that is, they are doubly occupied in all configuration state functions(CSFs). Unlike the core orbitals, these orbitals are completely optimized. If the CLOSED card is missing, then data corresponds to that of the most recent MCSCF calculation, or else the atomic inner shells.

3.3.4 Characterizing the state symmetry

The symmetry of each state to be optimized is defined by one WF card. The number of electrons and total symmetry of the wavefunction are defined on the WF card:

WF, *elec*, *sym*, *spin*

The definition of the options is the same as used in the SCF calculation.

3.3.5 Specifying the number of states in the present symmetry

The input directive STATE always checks the state symmetry as specified on the previous WF card and is given by STATE, *nstate*;

nstate defines the number of states in the present symmetry.

3.3.6 Characterizing the initial guess

MULTI always needs an initial orbital guess. The initial guess is represented as

START, *orb*, *ci*, *option*;

orb defines the record name for the starting orbitals. If this is absent, the program tries to search for suitable starting orbitals by three methods as follows.

First, the program tries to check orbitals from the record specified on the ORBITAL card (or the corresponding default). All files are searched.

Second, the program attempts to identify orbitals from the most recent MCSCF calculation. All files are searched. Third, the program tries to identify orbitals from the most recent SCF calculation. All files are searched. If no orbitals are found, an error exit occurs.

ci represents the record name for initial CI-coefficients. This is only available if the CI-vectors have been saved in a previous MULTI calculation using the same

configurations by specifying CI and *cidump* on a NATORB, CANONICAL or LOCALI card which will be described later in the following sub-sections.

option describes that if *option* is equal to CANONICAL, the initial orbitals are canonicalized. This sometimes improves convergence but needs some spare computational capacity.

3.3.7 Saving the final orbitals

The command is ORBITAL, *record.file*

The final orbitals are dumped to record *record.file*. Default for *record* corresponds to 2140 and *file* to 2. This record number is increased by one for each following MCSCF calculation in the same job. In the presence of a NATORB, CANONICAL or LOCALI card, the ORBITAL card can be absent because *orb* can also be set on these cards.

3.3.8 Natural orbitals

This command is of the form

NATORB, *orb*, *option*, *cidump*, *state*, *print*;

It is employed to compute the final natural orbitals and write them to record.*orb*.

If *option* is equal to CI, then the hamiltonian is diagonalized using the new orbitals, and the CI-coefficients greater than 0.04 are printed.

If *cidump* is specified, the new CI vectors are saved to this record. The natural orbitals are obtained by default and saved on the record provided on the ORBITAL card or the default record as represented by ORBITAL.

If *state* is given in the form *istate.istsym*, the natural orbitals are obtained for this state. *istsym* represents the sequence number of the corresponding WF card in the input, and *istate* accounts for the state number in that state symmetry.

print expresses the number of virtual orbitals to be printed in each symmetry.

3.3.9 Pseudo-canonical orbitals

The directive is specified by

CANONICAL, *orb*,*option*,*cidump*,*state*,*print*;

It is used to canonicalize the final orbitals, and write them to record *orb*. All options are the same for NATORB

3.3.10 Localized orbitals

The command is expressed with

LOCALI, *orb*,*option*,*cidump*,*state*,*print*;

It is used to localize the final orbitals and store them on record *orb*. All options are the same for NATORB mentioned earlier.

3.3.11 Maximum number of iterations

The command is

MAXITER, *maxit*;

maxit defines maximum number of iterations. If the calculation has not converged in the default number of iterations, one should consider the reason before increasing the number of iterations. In most cases the active orbitals or the optimized states have not been chosen suitably.

3.3.12 The input files and the description of the directives for MCSCF(CASSCF)

In this work we have considered five cases, namely NF^+ , PCl^+ , AsCl^+ , BBr^+ and $\text{HC} + \text{NO}$ as mentioned earlier in the introduction chapter.

3.3.12.1 The input file and the descriptions of the terms for NF^+

The input file for the $^2\Pi$ state with the valence quadruple-zeta (VQZ) basis sets for NF^+ is shown as follows.

*****, The MCSCF (CASSCF) calculation for the NF^+ excited states**

file,2,nfplus.wfu,new

zmat,angstrom

N

F,N,r

endz

basis=vqz

r=1.1

int;

rhf;wf,15,2,1;

text,CASSCF, state averaged orbitals for Π states

multi;occ,6,2,2;closed,2,0,0;start,2130.2;orbital,2140.2;natorb,,ci;

wf,15,2,1;state,2;wf,15,3,1;state,2;maxiter,15;

ci;wf,15,2,1;state,2;

The description of the directives is given.

1) *** means to start a job. The first card of each input should be specified by

***, *text*

where *text* can be anything. The effect of this card is to reset all program counters, etc. If the *** card is missing, it is assumed that text is its default value, which means all blank.

2) , (comma) means to move to next tab stop.

3) ; (semicolon) means the end of record.

4) File

MOLPRO treats three sequential text files which are the *input file*, the *output file* and the *punch file*. The punch file shows a short form of the output which contains the most important data and results, namely geometries, energies, dipole moments and so on. Moreover, there exist up to 9 binary MOLPRO files available. Each one can correspond to the program simply by its number (1 to 9) respectively. By default, they are temporary files which are generally assigned actively by the program but they are able to be linked to permanent files with the FILE command. File 1 corresponds to the main file with basis set, geometry, and the one and two electron integrals. By default, file 2 is the dump file and utilized to keep the wavefunction information, for example orbitals, CI coefficients and density matrices. File 3 is an auxiliary file which can be utilized with File 2 for restart purposes. File 4 to 8 are allowed as scratch space, for instance, for sorting the integrals, storage of transformed integrals and of the CI vectors.

The File directive is defined by

File, *file*, *name*, [*status*]

file means the logical MOLPRO file number (1 - 9) mentioned above. *name* is the file name. *status* can be one of the terms, namely UNKNOWN, OLD, NEW,

ERASE, SCRATCH and DELETE

UNKNOWN shows if a permanent file opened exists it is automatically restarted.

OLD is the same as UNKNOWN.

NEW describes that if a permanent file opened exists it is overwritten and not restarted.

SCRATCH: If a temporary file opened exists, it is erased and not restarted. After the job is completed, the file no longer exists.

DELETE is the same effect as SCRATCH.

For example, file, 2, nfplus.wfu, new assigns permanent file 2 with name nfplus.wfu.

All previous information on the file is eliminated.

5) Record

Record names are positive integers and are generally set in the format *record.file*, e.g., 2100.1 represents the record called 2000 on file 1. It is noted that record names are quite random, and their numerical values have no relationship with the order of the records in the file.

6) --- (three dashes) means the end of a job and also, an end of file can end a job

Alternatively, a job can be finished at some place by adding an EXIT card.

7) Assigning dynamic memory (MEMORY)

The directive is expressed of the form

MEMORY, *n*, *scale*;

This directive sets the limit on dynamic memory to *n* floating point words.

If *scale* is defined as K, *n* is multiplied by 1000. If *scale* is given as M, *n* is multiplied by 1 000 000.

The MEMORY card must be located before all FILE cards.

For example a , MEMORY, 4, M card will allocate 4 000 000 words of momory.

8) DO loops (DO/ENDDO)

DO loops can be formed with the DO and ENDDO commands. The general format is defined in the form

DO variable = start, end [[,] increment] [[,] unit]

where *start*, *end*, *increment* may be expressions or variables. Every DO should finish with its own ENDDO.

9) VARIABLES

Variables originally can be defined with the SET command but to be simple and more flexible the directive is specified with an equal sign as shown.

SET, variable, expression [,] [unit], . . . is altered to

variable = expression [,] [unit], . . .

unit represents an optional string, which can be utilized to link a unit to a variable.

For instance, R = 2.0 ANG, THETA = 180 DEGREE specify the variables R and THETA.

Variables can be indexed, but only one-dimensional arrays(vectors) are allowed.

Vectors(arrays) can be reasonably specified with square brackets as in the example.

R = [1.0, 1.2, 1.3] ANG, THETA = [120, 130, 140] DEGREE

The current length of an array can be represented by putting # before the variable name (e.g. #R).

10) TEXT, xxxxxx means to print xxxxxx in the output.

11) INT defines to call the machine default integral program.

12) Symmetry specification

ZMAT is used to define the Z-matrix. If standard Z-matrix input is chosen,

MOLPRO-94 adopts the symmetry of the molecule automatically by default.

However, sometimes it is reasonable to use a lower symmetry or a different orientation than given by the default. MOLPRO can only make use of Abelian point group symmetry. For molecules with degenerate symmetry, an Abelian subgroup should be allowed for linear molecules, for instance, C_{2v} or D_{2h} .

The symmetry group utilized is specified for the integral input with combinations of the symmetry elements x , y and z , which characterize which coordinate axes change sign under the corresponding producing symmetry operation. Generally it is usual to select z to be the specific axis where suitable.

13) Geometry specifications

The geometry specifications are represented in the form

ZMAT, *options*

atom specifications

ENDZ

The following terms, namely NOSYM, ANGSTROM, CHARGE, MASS and NOORIENT are allowed as options.

NOSYM means the disable use of the symmetry.

ANGSTROM shows that the bond lengths defined by numbers or variables with no associated units are supposed to be in Å.

CHARGE specifies that the molecule be oriented such that the origin is the center of charge, and the axes are eigenvectors of the quadrupole moment.

MASS defines the orientation of molecule such that the origin is the center of mass, and the axes are eigenvectors of the inertia tensor (default).

NOORIENT specifies that be disabled re-orientation of the molecule.

14) Z-matrix input

An atom specification is generally given in the form as follows.

$[group[,]] atom, P_1, r, P_2, \alpha, P_3, \beta, J$

or alternatively,

$[group[,]] atom, P_1, x, y, z$

group means the atomic group number(optional).

atom represents the chemical symbol of the new atom placed at position P_0 .

P_1 shows the atom to which the present atom is connected.

r is the distance of the new atom from P_1 .

P_2 is a second atom required to define the angle $\alpha(P_0, P_1, P_2)$.

α is the internuclear angle $\alpha(P_0, P_1, P_2)$ and should be in the range $0 < \alpha < 180^\circ$.

P_3 is a third atom required to specify the dihedral angle $\beta(P_0, P_1, P_2, P_3)$.

β means the dihedral angle $\beta(P_0, P_1, P_2, P_3)$ in degree and this angle is characterized

as the angle between the planes specified by (P_0, P_1, P_2) and (P_1, P_2, P_3)

$(-180^\circ \leq \beta \leq 180^\circ)$.

15) Default basis sets

The basis set may either be obtained from the program or be defined in the input, or any combination of the two.

If a basis is not specified for any specific atom group, then the program adopts a default. At present, this default takes VDZ and may be overridden with BASIS, *basis*

The program then produces requests for s, p, d, . . . (to a suitable maximum) sets from the library under the key name *basis* and also utilizes the default contraction

scheme in the library. For instance, BASIS = VQZ specifies valence quadruple-zeta basis sets for all atoms.

Default basis sets can be specified with one or more BASIS cards before the integral input. One line input of a global default basis set is of the form

BASIS, *basisname*

where *basisname* represents a valid basis set name from the basis library.

Alternatively, a global default basis can be defined as

BASIS = *basisname*

For this default *basisname* is saved in variable BASIS.

In individual atoms default basis sets can be characterized, for example, as

BASIS, O=VTZ, H=VDZ

This leads the default basis for oxygen to VTZ and for hydrogen to VDZ.

The first two forms can be combined of the form

BASIS, VTZ, O=AVTZ, H=VDZ

This specifies the global default VTZ overwritten by other basis sets for oxygen and hydrogen.

We have considered the six states for each of the diatomic molecular ions as mentioned earlier in the introduction.

For five other states, namely $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$ and $^4\Pi$ the number of the irreducible representation and the spin symmetry of the wavefunction specified on the WF card are changed as follows.

wf,15,1,1 for $^2\Sigma^+$, wf,15,4,1 for $^2\Sigma^-$, wf,15,1,3 for $^4\Sigma^+$, wf,15,4,3 for $^4\Sigma^-$ and wf,15,2,3;wf,15,3,3 for $^4\Pi$

More details for the input files will be shown in the APPENDIX A.

Thus, we have carried out calculations for the five other states described above with the same basis sets and the same procedure as above.

In other calculations we have used the VDZ and VTZ basis sets , for the each of the six $^2\Pi$, $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$ and $^4\Pi$ states. The calculations have been performed by the same method as above.

3.3.12.2 The input file with the description of the commands for PCI^+

The calculation for the $^2\Pi$ state with the vqz basis sets for PCI^+ is given as an example of the six jobs we have considered for PCI^+ .

***, The MCSCF(CASSCF) for the PCI^+ excited states

file,2,pclplus.wfu,new

zmat,angstrom

p

cl,p,r

endz

basis=vqz

r=2.0

int;

rhf;wf,31,2,1;

text,CASSCF, state averaged orbitals for PI states

multi;occ,10,4,4;closed,6,2,2;start,2130.2;orbital,2140.2;natorb,,ci;

wf,31,2,1;state,2;wf,31,3,1;state,2;maxiter,15;

ci;wf,31,2,1;state,2;

The description of the directives is the same as for NF^+ .

For other five states, namely $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$ and $^4\Pi$, the number of the irreducible representation and the spin symmetry of the wavefunction defined on the WF card are changed as follows.

The **wf,31,1,1;** , **wf,31,4,1;** , **wf,31,1,3;** , **wf,31,4,3;** and **wf,31,2,3;wf,31,3,3;** correspond to the $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$ and $^4\Pi$ states respectively (More detailed descriptions of the input files will be given in the APPENDIX A). Thus, the five other calculations with the vqz basis sets have been performed by the same method as above. Also, for the six states mentioned above, calculations above have been carried out with the VDZ and VTZ basis sets.

3.3.12.3 The input file with the description for AsCl^+

We have made two sets of calculations for AsCl^+ , namely calculations with effective core potentials and all electron calculations.

There are two input files, depending on which basis set we have used.

A) The $^2\Pi$ state with the vqz basis sets is given as an example of the six calculations with effective core potentials (ECP).

*****, The MCSCF(CASSCF) with ECP for the AsCl^+ excited states**

file,2,asclplus.wfu,new

zmat,angstrom

```

as
cl,as,r
endz
r=2.0
int;
ecp,1,ecp28mwb;
sp,1,ECP28mwb;c;
d,1,0.2;
spd,2,vqz;c
rhf,wf,21,2,1;save,2130.2;
multi,start,2130.2;orbital,2140.2;wf,21,2,1;state,2;wf,21,3,1;state,2;maxiter,20;
ci,maxiter,30;wf,21,2,1;state,2;
---
```

The description of the commands is provided.

1) Effective core potentials

The pseudopotentials (effective core potentials, ECPs) are defined by the general form

ECP, i , . . . *< ECP specification >*

which specifies a pseudopotential for atom number i . The *< ECP specification >* can be composed either of a single keyword, which references a pseudopotential kept in the library or else of an explicit definition.

2) Input from ECP library

We have used pseudopotentials from the MOLPRO library. We have used the effective core potentials of Bergner *et al.* [154] for the 28 core electrons 1s 2s 2p 3s

3p 3d (library keyword ECP28mwb) and a double-zeta basis set for the 4s and 4p orbitals of As in which 4s 4p functions were contracted to 2s2p (directive sp,1,ECP28mwb;c;). This basis set for As was augmented with a set of d functions with exponent $0.2 a_0^{-2}$.

As mentioned in the previous two sections, for the calculations for the five other states, the wavefunction is defined on the WF card as follows.

The directives **wf,21,1,1;** , **wf,21,4,1;** , **wf,21,1,3;** , **wf,21,4,3;** and **wf,21,2,3;wf,21,3,3;** correspond to the $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$ and $^4\Pi$ states respectively (The input files will be detailed in the APPENDIX A). Calculations have been performed for these five states with the vqz basis set and also for each of the six states described above the calculations have been carried out with the vdz and vtz basis sets.

B) Input file for the $^2\Pi$ state with the density matrix averaged atomic natural orbital spd basis sets of Pierloot *et al.* [32] for all electron calculations.

The paper of Pierloot *et al.* [32] did not include **f functions**. We have included a set of **f functions** on each atom with orbital exponents obtained in approximate optimization calculations. The following input was used for explicit specification of the contraction coefficients.

```
basis={
s,As,566875.27,81319.075,23570.858,8145.6899,3020.1475,1159.8514,454.46921,
180.32733,72.153149,29.039871,11.737766,4.7595370,1.9346930,0.78795000,
0.32140800,0.13126800,0.05366800;

p,1.17,.00020296,.00142976,.00489810,.01685274,.05201895,.14368741,.31497391,
.39217752,.15110734,.06433589,.06541718,.00303928,.00932769,-.0016440,
.00137255,-.0006586,.00019134;
```


c,1.17,-.0000861,-.0006076,-.0020857,-.0072370,-.0227408,-.0660142,-.1630407,
-.2734087,-.1113708,.52958738,.48428439,.08238325,.12008913,.00079778,
.00742309,-.0036375,.00107870;

c,1.17,.00003590,.00025278,.00087249,.00301869,.00963277,.02831027,.07396927,
.13515051,.06434121,-.4432611,-.6137746,.48191430,.75698131,.09672850,
.00303073,-.0019214,.00076999;

c,1.17,-.0000072,-.0000503,-.0001748,-.0006002,-.0019393,-.0056726,-.0152215,
-.0281971,-.0149898,.11167210,.16948643,-.1742474,-.4547235,-.1026787,
.66642773,.50801138,.06456990;

c,1.17,.00000713,.00004970,0.00017498,0.00058929,0.00194799,.00556040,
.01534656,.02744414,.01670189,-.1180579,-.1591452,.15779656,.61302239,
-.0909193,-1.697669,.85494505,.73810089;

c,1.17,-.0000103,-.0000702,-.0002566,-.0008186,-.0028817,-.0076834,-.0229047,
-.0369944,-.0312064,.19562927,.18050605,-.1329016,-1.539666,2.3732698,
.01836764,-2.586834,1.9067495;

c,1.17,.00001317,.00009197,.00032287,.00109277,.00359410,.01034610,.02845364,
.05187448,.02952087,-.2387089,-.3133723,.51190610,1.8337359,-5.398318,
6.8845047,-5.373312,2.1489474;

c,1.17,-.0000292,-.0002345,-.0006191,-.0031013,-.0063641,-.0306351,-.0478022,
-.1818140,.10689378,.21951813,1.8157045,-5.766332,7.7571145,-6.760525,
4.5743538,-2.410163,.74939609;

c,1.17,.00007520,.00038299,.00229896,.00308781,.02871590,.02558548,.25430127,
.05757096,.60598964,-4.128541,7.0656387,-6.874868,5.0199110,-3.164701,
1.7956501,-.8502654,.24592800;

p,As,7323.1673,1790.4187,661.74735,271.20663,115.83947,50.511115,22.286680,
9.9062400,4.4249560,1.9833750,.89122700,.40122500,.18089000,.08164600,
.03688500;

c,1.15,.00047561,.00350535,.01483336,.05650420,.16920752,.36091932,.40886256,
.15600183,.01881103,.01114795,.00118334,.00068037,-.0003361,.00016669,
-.0000506;

c,1.15,-.0001969,-.0014538,-.0062188,-.0241014,-.0751389,-.1696334,
-.1967608,.10585183,.49687654,.43564024,.10502834,.00292970,.00124841,
-.0002971,.00010210;

c,1.15,.00004141,.00030506,.00131171,.00508090,.01600063,.03635452,.04258706,
-.0326435,-.1343777,-.1427463,.02398513,.32948097,.46992299,.24735085,
.09755815;

c,1.15,-.0000353,-.0002602,-.0011169,-.0043349,-.0136323,-.0310466, -.0363561,
.02789112,.11825328,.12608235,.00601399,-.5898859, -.2309490,21176561,
.84012370;

c,1.15,.00005512,.00038004,.00176842,.00631422,.02151037,.04487526,.06198377,
-.0594246,-.1462134,-.3280358,.31169970,1.1122965,-.7533416, -1.225132,
1.3006783;

c,1.15,-.0000823,-.0005170,-.0026858,-.0085671,-.0326318,-.0606250, -.1016352,
.13085313,.15145529,.74920079,-1.809454,.29029826,2.3248403, -3.049746,
1.4897966;

c,1.15,.00010704,.00088352,.00333244,.01486946,.04163625,.11035992,.09155739,
-.1075601,-.5924368,-.1936158,2.9827634,-5.122157,5.2233660, -3.575774,
1.3083317;

c,1.15,-.0001711,-.0021478,-.0047620,-.0369509,-.0645643,-.2875883,.02681609,
-.0268929,2.3862710,-5.055586 ,5.6307125,-4.693649,3.2656687, -1.788236,
.57746485;

c,1.15,.00062027,.00175953,.02293946,.03205212,.29379335,.19939782,.61869524,
-3.467027,5.2063666,-4.799614,3.5027558,-2.283633,1.3594583, -.6760427,
.20747854;

d,As,278.75717,85.080781,33.354708,13.920758,5.9571790,2.5813950,1.1266120,
.49389700,.21716600;

c,1.9,.00227463,.01718587,.07146928,.20721457,.35522274,.37056225,.22623647,
.05860114,.00565757;

c,1.9,-.0006527,-.0052431,-.0206010,-.0643699,-.1011768,-.1285510, -.0062769,
.31876083,.73696154;

c,1.9,.00080643,.00621466,.02535561,.07654012,.14152051,.16177215,.08719676,
-1.591518,1.3710081;

c,1.9,-.0001523,.01168293,-.0055750,.16569917,-.0481477,1.1566617, -2.765523,
2.4366394,-.9886865;

c,1.9,.00450086,-.0281167,.13253628,-.2518101,1.9057503,-3.042983,2.2441450,
-1.126087,.36478009;

f,As,0.5;

s,Cl,105818.82,15872.006,3619.6548,1030.8038,339.90788,124.53810,49.513502,
20.805604,6.4648238,2.5254537,.53783215,.19349716,.06772401;

c,1.13,.00030088,.00232977,.01200395,.04767388,.14650572,.32284149,.39830268,
.18514198,.03908065,.02732878,.00265779,-.0010655,.00032210;

c,1.13,-.0001008,-.0007766,-.0040646,-.0162047,-.0533804,-.1293144,-.2277685,
-.1055212,.52732620,.58926880,.04283083,-.0142461,.00423885;

c,1.13,.00002615,.00020215,.00105460,.00425383,.01407419,.03569705,.06574573,
.03577769,-.2323657,-.4041007,.66719688,.52351442,.02141530;

c,1.13,-.0000265,-.0002096,-.0010568,-.0044710,-.0138986,-.0387558,-.0627185,
-.0485623,.30897703,.39485922,-1.884600,1.3417293,.34453623;

c,1.13,.00003166,.00030139,.00113763,.00701933,.01246032,.07200651,.01940905,
.20239561,-.9690764,.62510060,1.2486084,-2.727998,1.9386491;

c,1.13,-.0000715,-.0006936,-.0025371,-.0163211,-.0275269,-.1716223,-.0454504,
-.4457992,2.7519939,-3.270030,2.5507227,-2.272800,1.0271748;

c,1.13,.00023307,.00084352,.01190370,.00718535,.21941115,-.0991755,2.0416878,
-4.109673,3.6805020,-2.102246,.86850535,-.5714372,.19801553;

p,Cl,589.77639,139.84860,44.794920,16.612069,6.5994980,2.7141323,.95279614,
.35804401,.12498600,.04374510;

c,1.10,.00293393,.02293778,.10200896,.27850180,.43936620,.31824231,.04761320,
-.0046048,.00260299,-.0006700;

c,1.10,-.0007964,-.0061995,-.0285906,-.0793268,-.1366825,-.0770651,.29967959,
.54772217,.29977172,.03737279;

c,1.10,.00074632,.00608487,.02670982,.08041079,.12030301,.11059197,-.5614517,
-.3963493,.74669657,.38289364;

c,1.10,-.0010334,-.0082977,-.0373785,-.1124823,-.1663478,-.1312383,1.2862180,
-1.045006,-.4043654,.92379800;

c,1.10,.00194582,.00995304,.07645655,.11813481,.47053356,-.6749759,-.6449575,
1.8487202,-2.039710,1.1971413;

c,1.10,-.0037388,-.0201912,-.1555785,-.2623020,-.7814880,2.3362096,-2.572716,
2.0838013,-1.340715,.59502235;

c,1.10,.00323560,.08972159,.17953539,1.4798753,-3.035690,2.5837958,-1.519641,
.87264654,-.4274141,.15522853;

d,Cl,1.5510000,.62800000,.25400000,.08890000;

c,1.4,.20266095,.54447101,.37843168,.03637670;

c,1.4,-.4301070,-.6134587,.96114253,.19412996;


```
c,1.4,1.0668065,-.9881785,-.1476311,.80660634;
```

```
c,1.4,-1.117806,1.9705270,-1.904159,1.1696891;
```

```
f,Cl,0.75}
```

*****, The MCSCF(CASSCF) calculation for the AsCl⁺ excited states**

```
memory,4,M
```

```
gprint,basis
```

```
file,2,ascl.wfu,new
```

```
zmat,angstrom
```

```
As
```

```
Cl,As,r
```

```
endz
```

basis={ Basis sets [32] and f functions inserted described above}

```
r=1.988
```

```
int;
```

```
rhf,wf,49,2,1;save,2130.2;
```

```
multi,start,2130.2;orbital,2140.2;wf,49,2,1;state,2;
```

```
wf,49,3,1;state,2;natorb,,ci;maxiter,20;
```

```
ci;wf,49,2,1;state,2;maxiter,30;
```

```
---
```

The description of the commands is given.

1) Global Print Options

The directive GPRINT, BASIS means print the basis set information.

2) Default basis sets

The simple form of basis set specification mentioned in the section 3.3.12.1 for

NF⁺ cannot modify contraction patterns or define individual basis function types.

However, this program accepts basis sets defined by the user.

3) Defining primitive basis sets

In the calculations for AsCl^+ the basis set was input using the following directives.

type, atom, exp1, exp2, . . . expn; expn + 1, . . . ;

for general specification of exponents.

4) Specifying the contraction

C, first.last, c1, c2, . . . cn; cn+1, . . . ;

C specifies the general specification of a contracted function. *first.last* specifies the range of primitives to be contracted. *c1, c2, . . .* defines the contraction coefficients.

For the five other states the wavefunctions on the WF card are represented by the same method as described previously. **The directives wf,49,1,1; , wf,49,4,1; , wf,49,1,3; , wf,49,4,3; and wf,49,2,3;wf,49,3,3;** correspond to the $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$ and $^4\Pi$ states, respectively. More detailed information for the input files is given in the APPENDIX A. The calculations with the basis sets above have been performed by the methods described previously.

3.3.12.4 The input file with the description for BBr^+ calculations.

As in the case of AsCl^+ , two input files are used, depending on the basis sets used.

A) The input file for the $^2\Sigma^+$ using the vqz basis set for B is with an effective core potential for Br

'', The MCSCF(CASSCF) with ECP for the BBr^+ excited states**

file,2,bbrplus.wfu,new

zmat,angstrom

br

b,br,r

endz

r=2.0

int;

ecp,1,ecp28mwb;

sp,1,ECP28mwb;c;

d,1,0.2;

spd,2,vqz;c

rhf,wf,11,1,1;save,2130.2;

multi;start,2130.2;orbital,2140.2;wf,11,1,1;

ci;maxiter,25;wf,11,1,1;

The explanation of the directives is the same as for AsCl⁺.

For the calculations for the five other states the wavefunction specification on the WF card will be as follows.

The directives wf,11,2,1;wf,11,3,1; , wf,11,4,1; , wf,11,1,3; , wf,11,4,3; and

wf,11,2,3;wf,11,3,3; are for the ²Π, ²Σ⁻, ⁴Σ⁺, ⁴Σ⁻ and ⁴Π states, respectively. With

the same basis sets calculations have been carried out for the five other states in the CI

calculations (More detailed input files will be shown in the APPENDIX A). By the

same procedure calculations with the vdz and vtz basis sets have been performed as

before for the six states in the CI calculations.

B) The input file for the $^2\Sigma^+$ state is given using the density matrix averaged atomic natural orbital spd basis sets of Pierloot et al. [32] for all electron calculations.

The basis sets [32] mentioned also did not involve f functions as for AsCl^+ . Thus, we have considered a set of **f functions** on each atom with orbital exponents derived in approximation optimization calculations.

The basis sets [32] and **f functions** are as follows.

```
basis={
s,b,3733.3327,561.19773,128.74655,37.055525,12.328842,4.5244350,1.7512670,
.33110600,.10371400,.03630000;

c,1.10,.00089506,.00685380,.03405961,.12149824,.30003476,.43780423,.24612184,
.01182080,-.0041555,.00140186;

c,1.10,-.0001843,-.0014446,-.0070458,-.0272609,-.0688604,-.1492362,-.1162892,
.59639270,.50850220,.0279295;

c,1.10,.00017375,.00145545,.00642290,.02889840,.05907191,.18733501,.05610638,
-1.266190,.71439434,.63133800;

c,1.10,-.0001905,-.0022532,-.0054437,-.0535594,-.0182450,-.4660871,.44113019,
1.1919254,-2.613045,1.8532640;

c,1.10,.00041293,.00635331,.00871287,.17192309,-.0360394,1.5479194,-2.597670,
2.0916662,-1.808131,.82628795;

c,1.10,-.0018783,-.0063398,-.1081313,-.2422706,-1.722278,3.4481013,-2.188265,
.81648507,-.5271625,.19778262;

c,1.10,.00116412,.03455897,.08663511,1.9799862,-3.771476,3.3066999,-1.551088,
.48391501,-.2951708,.10623095;

p,b,12.363854,2.6559950,.76067100,.24197800,.07787700,.02725700;

c,1.6,.01180214,.06978208,.25711950,.47791994,.31658558,.15418619;

c,1.6,-.0101247,-.0411527,-.2976093,-.4297342,.26234690,.76686529;

c,1.6,.01264464,-.0157798,.64934680,.05318564,-1.375829,1.1527377;
```

c,1.6,-.0414113,-.5027538,-.6687000,1.6112094,-1.444723,.68208364;
c,1.6,.10101989,1.2162674,-1.733241,1.5327407,-1.080771,.47514295;
c,1.6,-1.211295,1.0493365,-.7049688,.41881797,-.2220987,.08341775;
d,b,.84960000 .22760000 .06100000;
c,1.3,.26308016,.72852411,.21600414;
c,1.3,-.5392926,-.2061201,.91037494;
c,1.3,1.0076300,-1.107773,.70734273;
f,b,0.5;
s,br,726398.09,104397.37,30433.462,10587.659,3953.3311,1529.2687,603.64283,
241.30208,97.274404,39.445336,16.064020,6.5630990,2.6880510,1.1030880,
.45337500,.18657500,.07686000;
c,1.17,.00017178,.00120695,.00408286,.01402132,.04306166,.12106007,.27702660,
.39766198,.20124051,.06111923,.08253896,.00897909,.01154817, -.0007071,
.00132443,-.0006391,.00018715;
c,1.17,-.0000745,-.0005231,-.0017798,-.0061212,-.0192128,-.0558994,-.1424688,
-.2598491, -.1876112,.40046534,.56436765,.11656019,.14288156,.01737558,
.00488550,-.0024274,.00075578;
c,1.17,.00003235,.00022699,.00077451,.00266440,.00845045,.02495022,.06655876,
.13230398,.10968715,-.3296791,-.7175227,.24962720,.86077452,.16991921,
-.0009038,.00040351,.00025571;
c,1.17,-.0000070,-.0000486,-.0001670,-.0005703,-.0018305,-.0053803,-.0147186,
-.0297070,-.0267983,.08931551,.21571073,-.0983141,-.5401008, -.1813165,
.70032290,.52055942,.06829549;
c,1.17,.00000715,.00004950,.00017333,.00057515,.00190960,.00541264,.01541925,
.02965814,.03011788,-.1004945,-.2100857,.07186230,.75535126,.04288634,
-2.071636,1.2200300,.55775136;
c,1.17,-.0000099,-.0000662,-.0002464,-.0007460,-.0027544,-.0069555,-.0224916,
-.0369315,-.0525205,.17473534,.21859267,.06952823,-1.974930,2.7748771,
-.3066606,-2.416982,1.8979116;
c,1.17,.00001250,.00008626,.00030383,.00100033,.00335409,.00943369,.02726831,
.05238938,.05422871,-.2021210,-.3915908,.30445916,2.3618800, -5.871548,
7.1868256,-5.613372,2.2896328;

c,1.17, -.0000280,-.0002351,-.0005480,-.0031636,-.0053220,-.0313810,-.0404392,
-.2059670,.08970384,.02604439,2.4907667,-6.483602,8.0518936, -6.748147,
4.4906056,-2.359195,.73688996;

c,1.17,.00007465,.00033662,.00239109,.00202747,.03021038,.01389412,.27310803,
.02437234,.94485222,-4.696051,7.3584269,-6.828337,4.8618486, -3.026917,
1.7067841,-.8049559,.23186565;

p,br,8403.9531,2045.4876,758.03053,312.04749,133.97148,58.739849,26.065724,
11.653786,5.2364600,2.3611850,1.0674040,.48345700,.21929300,.09958500,
.04526500;

c,1.15,.00046552,.00344657,.01448760,.05497741,.16467531,.35401911,.40889330,
.16390226,.02387166,.01450093,.00145392,.00077524,-.0003901,.00019884,
-.0000594;

c,1.15,-.0002019,-.0014988,-.0063627,-.0245837,-.0765807,-.1744477,-.2065083,
.09642479,.50763697,.44024688,.09105334,.00385376,.00039586,.00040310,
-.0000474;

c,1.15,.00004878,.00036154,.00154208,.00596297,.01877038,.04315088,.05155680,
-.0367497,-.1651611, -.1757596,.08337046,.40615221,.43618749,.20984350,
.05198536;

c,1.15,-.0000471,-.0003426,-.0014963,-.0056479,-.0182200,-.0408242, -.0512209,
.04076137,.15468719,.20456982,-.1413285,-.7753680,.00839657,.57202129,
.45567604;

c,1.15,.00006567,.00043866,.00212041,.00720896,.02576808,.05168330,.07849861,
-.0833837,-.1617296,-.4603510,.79636922,.83943767,-1.577329, -.0575172,
.93186903;

c,1.15,-.0000948,-.0006663,-.0030387,-.0110089,-.0372889,-.0803868,-.1068504,
.12944724,.31791600,.62110311,-2.504650,2.2167830,.19657112,-1.966279,
1.3686334;

c,1.15,.00009808,.00105671,.00283882,.01782377,.03681488,.13648227,.04128120,
.00040876,-1.001147,.91873232,1.3438470,-3.913516,5.0720542, -4.166387,
1.7672018;

c,1.15,-.0001847,-.0020133,-.0053883,-.0344011,-.0726888,-.2665294,-.0279251,
.15055815,2.0530371,-4.876015,5.9431241,-5.441049,4.1631221,-2.500616,
.8758621;

c,1.15,.00061209,.00185793,.02244420,.03364321,.29569803,.19718748,.61841056,
-3.513321,5.4005450,-5.151123,3.9197069,-2.677040,1.6724870,-.8698927,
.27671479;


```

d,br,346.90938,105.80051,41.951391,17.762403,7.7206840,3.4002370,1.5087570,
.67261300,.30079300;

c,1.9,.00204694,.01576190,.06621436,.19722095,.35363595,.38126361,.22345427,
.05042297,.00490447;

c,1.9,-.0005985,-.0049319,-.0194409,-.0627117,-.1040900,-.1346464,-.0051688,
.33992578,.71786505;

c,1.9,.00070312,.00586860,.02262035,.07575085,.14022494,.19577494,.03124856,
-1.572874,1.3919646;

c,1.9,-.0003282,.01114682,-.0118131,.16516036,-.0493016,1.2016808,-2.885191,
2.5971846,-1.070199;

c,1.9,.00392103,-.0347592,.11538079,-.2835994,2.0338858,-3.233039,2.4384676,
-1.248180,.40626142;

f,br,0.75}

***, MCSCF(CASSCF) for BBr+ excited states for all electron calculations

memory,4,M

gprint,basis

file,2,bbr.wfu,new

zmat,angstrom

B

Br,B,r

endz

basis={Basis sets [32] and f functions introduced above}

r=2.5

int;

rhf,wf,39,1,1;save,2130.2;

multi,start,2130.2;orbital,2140.2;wf,39,1,1;state,6;natorb,,ci;maxiter,20;

ci;wf,39,1,1;maxiter,30;

---
```

The directives have already been described in the previous three sections.

For the following five MCSCF calculations, the wavefunctions on the WF card are specified as before.

The directives **wf,39,2,1;wf,39,3,1; , wf,39,4,1; , wf,39,1,3; , wf,39,4,3; and wf,39,2,3;wf,39,3,3;** correspond to the $^2\Pi$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$ and $^4\Pi$ states, respectively.

The calculations have been carried out as usual for the five other states in the CI calculations and more detailed input files are described in the APPENDIX A.

3.3.12.5 The input file for the calculations for HC + NO

We have considered two input files, depending on the geometry treated.

A) The $^1\Sigma^+$ state using the vdz basis sets with the linear geometry

*****, MCSCF (CASSCF) for HC + NO 1-Sigma-Plus**

memory,4,M

file,2,hcno.wfu,new

zmat,angstrom

h

c,h,rch

n,c,rcn,h,180

o,n,rno,c,180

endz

basis=vdz

rch=1.058

rcn=1.500

rno=1.198

int;

rhf,wf,22,1,0;

text,CASSCF, state averaged orbitals for 1SIG+ states

multi,occ,10,3,3;closed,5,0,0;start,2130.2;orbital,2140.2;natorb,,ci;

wf,22,1,0;maxiter,25;

ci;occ,10,3,3;core,6,0,0;wf,22,1,0;maxiter,25;

We have considered the four states, namely $^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$ and $^3\Sigma^-$ in this work. Thus, for other the three states, the wavefunctions defined on the WF card is specified as follows.

The directives **wf,22,4,0;** , **wf,22,1,2;** and **wf,22,4,2;** are for the, $^1\Sigma^-$, $^3\Sigma^+$ and $^3\Sigma^-$ states, respectively. The orbitals obtained with the vdz basis sets were used in the subsequent CI calculations.

B) The $^1A'$ state using the vdz basis sets with the bent geometry

*****, MCSCF (CASSCF) for HC + NO $^1A'$ state**

memory,4,M

file,2,hcno.wfu,new

zmat,z,angstrom

h

c,h,rch

n,c,rcn,h,180

o,n,rno,c,180


```

endz

basis=vdz

rch=1.058

rcn=1.750

rno=1.198

int;

rhf,wf,22,1,0;

text,CASSCF, state averaged orbitals for 1A' states

multi,occ,13,3;closed,5,0;start,2130.2;orbital,2140.2;natorb,,ci;

wf,22,1,0;maxiter,25;state,2;

ci;occ,13,3;core,6,0;wf,22,1,0;maxiter,25;

---
```

This calculation is in C_s point group symmetry with this **Z** generator and the number of the irreducible representations in the two dimensional group is 2 (A' which is s, x, y, yz and A'' which is z, xz, yz). Thus, the π orbitals in the plane of the molecule are of the same symmetry as the sigma orbitals.

For calculations for A'' or triplet states, the WF card should be changed to specify the state of interest. However, those calculations have not been performed due to lack of time and are left for further work.

3.4 CI calculation

The command CI or CI-PRO calls the program for single and double excitations. The command CISD specifies a fast closed-shell CISD program. The command QCI calls a closed-shell quadratic CI program. The command CCSD calls closed-shell coupled-cluster program.

The internally contracted MRCI program is directed by the CI command.

For special cases, this includes single reference CI, CEPA, ACPF and MR-ACPF calculations. For closed-shell reference functions, a special faster code is used, which can be requested with the CISD, QCI or CCSD commands. This also includes the calculation of Brueckner orbitals for all three cases (QCI and CCSD are the same in this case).

Without further input cards, the wavefunction definition (core, closed, and active orbital spaces, symmetry) is the one used in the most recent SCF or MCSCF calculation. By default, a CASSCF reference space is produced. In the absence of an ORBITAL directive, the orbitals are obtained from the corresponding SCF or MCSCF calculation. The wavefunction may be saved with the SAVE directive and restarted with the START directive. The EXPEC directive enables one to calculate expectation values over one-electron operators, and the TRAN directive can be used to calculate transition matrix elements for one-electron properties.

The NATORB directive can be used to print and to save natural orbitals.

3.4.1 Occupied orbitals

The directive is of the form

OCC, n_1, n_2, \dots, n_8 ;

n_i defines numbers of occupied orbitals (involving CORE and CLOSED) in irreducible representation number i . If not present, by default the information is obtained from the most recent SCF, MCSCF or CI calculation.

3.4.2 Frozen-core orbitals

The command is given by

CORE, n_1, n_2, \dots, n_8 ;

n_i specifies the number of frozen-core orbitals in irrep number i . The orbitals are doubly occupied in all configurations and not correlated. If no CORE is present, the program uses the same core orbitals for the last CI calculation; If there were none specified the atomic inner shells are used for core. To override this and correlate all the electrons, the specification of a CORE card is required.

3.4.3 Closed-shell orbitals

The directive is expressed by

CLOSED, n_1, n_2, \dots, n_8 ;

n_i specifies the number of closed-shell orbitals in irrep number i including any core orbitals. These orbitals do not form part of the active space, that is, they are doubly occupied in all reference CSF's. However, compared to the core orbitals, these orbitals are correlated with single and double excitations. If the CLOSED card is absent, by default the information is obtained from the most recent SCF, MCSCF or CI calculation.

3.4.4 Specifying the orbitals

The command is of the form

ORBIT, *name.file*;

name.file is the record from which orbitals are read. By default the set of orbitals is generated from the last SCF, MCSCF or CI calculation.

3.4.5 Specifying the state symmetry

The information defined on the WF card is the same as used for a SCF or MCSCF calculation. The WF card should be located after any cards specifying the orbital spaces (OCC, CORE, CLOSED).

3.4.6 Specifying state numbers

The command is described by

STATE, *nstate*, *nroot(1)*, *nroot(2)*, . . . , *nroot(nstate)*;

nstate shows the number of states to be considered simultaneously and *nroot(i)* determine the root numbers to be calculated. These are used for the order of the states in the initial CI. If not defined, $nroot(i) = i$. All states defined should be reasonably accounted for by the internal configuration space. It is possible to have different convergence thresholds for each state. It is also possible not to optimize some lower roots which are involved in the list *nroot(i)*.

3.4.7 Maximum number of iterations

The directive is MAXITER, *maxit*, *maxiti*;

maxit is the maximum number of macroiterations and *maxiti* is the maximum number of microiterations (internal CI).

3.4.8 Saving the wavefunction

The command is SAVE, *savecp*, *saveco*, *idelcg*;

savecp is the record name for saving the wavefunction. *saveco* is the record name for saving the internal configurations and their maximum weight over all states for subsequent use as reference input. *idelcg* shows if nonzero icfil and igfil (holding CI and residual vectors) remains at the end of the calculation.

3.4.9 Starting wavefunction

The command is START, *readc1*, *irest*;

readc1 is the record name from which the wavefunction is restored for a restart.

irest , if nonzero, indicates that the CI coefficients are read and used for the restart; otherwise, only the wavefunction definition is interpreted.

3.4.10 Transition moment calculations

The directive is TRANS, *readc1*, *readc2* (*oper(i)* = 1, 7);

Instead of carrying out an energy calculation, only the calculation of the transition matrix elements is performed between the wavefunctions saved on records *readc1* and *readc2*. At most 7 operator record names may be defined. With *oper(i)* negative, the operator is supposed to be antisymmetric. With no operator names specified the dipole transition moments are calculated. Symbolic operator names may be available rather than the record names.

3.4.11 The input files for CI

As in the case of MCSCF, we have made CI calculations for the five species mentioned and also for the diatomic molecular ions we have made transition moment calculations.

3.4.11.1 The input file for NF^+

Two input files are given, which are for the CI calculation and for the transition moment calculation.

A) The $^2\Pi$ state with the valence quadruple-zeta (VQZ) basis sets

*****, The CI calculation for the NF^+ excited states**

file,2,nfplus.wfu

zmat,angstrom

N

F,N,r(i)

endz

basis=vqz

r=[0.85,0.9,1.0,1.1,1.2,1.3,1.4,1.5,1.75,2.0,2.25,2.5,2.75,3.0,3.5,4.0,4.5]

do i=1,#r

int;

text,CASSCF, state averaged orbitals for PI states

multi;occ,6,2,2;closed,2,0,0;start,2140.2;orbital,2140.2;natorb,,ci;

wf,15,2,1;state,2;wf,15,3,1;state,2;maxiter,15;

ci;wf,15,2,1;state,2;

enddo

As mentioned earlier in the MCSCF calculation, five other states have been considered and the appropriate WF cards used. Then, the calculations have been performed, as usual, with the VQZ basis sets and for the six states all the energy values and graphs obtained from this work will be provided in the Results and Discussion (chapter4). With the VDZ and VTZ basis sets for each for the six states the calculations have been carried out by the same procedure above. Also, all the energies and graphs produced with the VDZ and VTZ basis sets will be given in the APPENDIX B.

B) The ${}^2\Pi$ (state,2) \rightarrow ${}^2\Sigma^+$ (state,5) transition moment calculations with the vqz basis sets.

*****, NF⁺ 2pi to 2sig⁺ transition moments**

memory,4,M

file,2,nfplus.wfu

zmat,angstrom

N

F,N,r(i)

endz

basis=vqz

r=[1.0,1.1,1.2,1.3,1.5,1.6,1.7,1.8,1.9,2.0,2.1,2.2,2.3,2.4,2.5]

do i=1,#r

int;

text,CASSCF, state averaged orbitals for 2PI to 2sig⁺ states

multi;occ,6,2,2;closed,2,0,0;start,2140.2;orbital,2140.2;natorb,,ci;

wf,15,1,1;state,5;

```

wf,15,2,1;state,2;wf,15,3,1;state,2;maxiter,15;

ci;occ,6,2,2;closed,2,0,0;wf,15,1,1;state,5;orbital,2140.2;natorb;

save,8000.2;

ci;occ,6,2,2;closed,2,0,0;wf,15,2,1;state,2;orbital,2140.2;natorb;

save,7000.2;

ci;trans,7000.2,8000.2;

enddo

---
```

Also, we have made another calculation which is for the ${}^4\Pi(\text{state},2) \rightarrow {}^4\Sigma^-(\text{state},3)$ transition moments for NF^+ with the same basis sets above. Thus, the input file is changed as follows.

The directives **wf,15,2,3;wf,15,3,3** for the ${}^4\Pi(\text{state},2)$ and **wf,15,1,3** for the ${}^4\Sigma^-(\text{state},3)$ are required. By the same sequence we have calculated the ${}^4\Pi(\text{state},2) \rightarrow {}^4\Sigma^-(\text{state},3)$ transition moments for NF^+ with the vqz basis sets. The graphs of the two transition moment calculations above will be shown in Chapter 4.

3.4.11.2 The input file for PCI^+

As in the case of NF^+ , two input files are shown.

A) The ${}^2\Pi$ state with the vqz basis set

***, The CI calculation for the PCI^+ excited states

```
file,2,pclplus.wfu
```

```
zmat,angstrom
```

```

p
cl,p,r(i)
endz

basis=vqz

r=[1.3,1.5,1.6,1.7,1.8,1.9,2.0,2.1,2.2,2.3,2.4,2.5,2.75,3.0,3.5,4.0,4.5]

do i=1,#r

int;

text,CASSCF, state averaged orbitals for PI states

multi,occ,10,4,4;closed,6,2,2;start,2140.2;orbital,2140.2;natorb,,ci;

wf,31,2,1;state,2;wf,31,3,1;state,2;maxiter,15;

ci;wf,31,2,1;state,2;

enddo

---
```

For the calculations for the other five states, the options on the WF card are reset as described previously for the MCSCF calculation for PCl^+ and the calculations carried out in the usual manner. All energies calculated and the graphs produced for the six states will be given in Chapter 4 (Results and discussion for PCl^+).

For both the VDZ and VTZ basis sets, calculations for the six states have been performed as before and all energy values and graphs obtained from the calculations are given in the APPENDIX B.

B) The $^2\Pi(\text{state},2) \rightarrow ^2\Sigma^+(\text{state},2)$ transition moments calculation for PCl^+

*****, PCl^+ 2pi to 2sig+ transition mementos**

file,2,pclplus.wfu

zmat,angstrom

p

cl,p,r(i)

endz

basis=vqz

r=[1.3,1.5,1.6,1.7,1.8,1.9,2.0,2.1,2.2,2.3,2.4,2.5]

do i=1,#r

int;

text,CASSCF, state averaged orbitals for 2PI to 2sig+ states

multi;occ,10,4,4;closed,6,2,2;start,2140.2;orbital,2140.2;natorb,,ci;

wf,31,1,1;state,2;

wf,31,2,1;state,2;wf,31,3,1;state,2;maxiter,15;

ci;occ,10,4,4;closed,6,2,2;wf,31,1,1;state,2;orbital,2140.2;natorb;

save,8000.2;

ci;occ,10,4,4;closed,6,2,2;wf,31,2,1;state,2;orbital,2140.2;natorb;

save,7000.2;

ci,trans,7000.2,8000.2;

enddo

For transition moments for the transition ${}^4\Pi(\text{state},2) \rightarrow {}^4\Sigma^-(\text{state},3)$ for PCl^+ , with the

same basis sets as above, the options on the WF card are changed to

wf,31,2,3;wf,31,3,3; and wf,31,4,3; corresponding to the ${}^4\Pi(\text{state},2)$ and ${}^4\Sigma^-(\text{state},3)$ states, respectively. By the usual method the ${}^4\Pi(\text{state},2) \rightarrow {}^4\Sigma^-(\text{state},3)$ transition moments have been calculated with the vqz basis sets. The figures for transition moments will be provided in Chapter 4.

3.4.11.3 The input file for AsCl^+

Three input files are required, which are for the basis sets using ECP, for the all-electron basis sets [32] and for the transition moments.

A) The input file for the ${}^2\Pi$ state is given with ECP using the vqz basis sets

*****, The CI calculation for the AsCl^+ excited states**

file,2,asclplus.wfu

zmat,angstrom

as

cl,as,r(i)

endz

r=[1.3,1.4,1.5,1.6,1.7,1.8,1.9,2.0,2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,3.0,3.5,4.0,4.5,5.0]

do i=1,#r

int;

ecp,1,ecp28mwb;

sp,1,ECP28mwb;c;

d,1,0.2;

spd,2,vqz;c

```

multi,start,2140.2;orbital,2140.2;natorb,,ci;wf,21,2,1;state,2;
wf,21,3,1;state,2;maxiter,20;
ci,maxiter,30;wf,21,2,1;state,2;
enddo
---
```

As in the two previous sections, calculations were made for the five other states with the wavefunctions defined on the WF card as in the MCSCF calculations.

Comparable calculations with the VDZ and VTZ basis sets for each of the six states have been performed as before. All the energies calculated and graphs generated with the VDZ, VTZ and VQZ basis sets will be given in the APPENDIX B.

B) The CI input file for the $^2\Pi$ state with the density matrix averaged atomic natural orbital spd basis sets of Pierloot *et al* [32] as an example.

*****, The CI calculation for the AsCl^+ excited states**

```

memory,4,M
gprint,basis
file,2,ascl.wfu
zmat,angstrom
As
Cl,As,r(i)
endz
```

basis={ The same basis sets [32] and f functions as used in the MCSCF }


```

r=[1.4,1.5,1.6,1.7,1.8,1.9,2.0,2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,3.0,3.1,3.2,3.3,3.5,4.0
,4.5,5.0]

do i=1,#r

int;

multi,start,2140.2;orbital,2140.2;wf,49,2,1;state,2;

wf,49,3,1;state,2;natorb,,ci;maxiter,20;

ci;wf,49,2,1;state,2;maxiter,30;

enddo

---
```

For the five other states the calculations were made with similar input files with the wavefunctions specified on the WF card as in the MCSCF calculations. All the energy values and graphs obtained from these calculations will be given in Chapter 4 (Results and discussion for AsCl^+) .

C) The input file for the ${}^2\Pi(\text{state},2) \rightarrow {}^2\Sigma^+(\text{state},2)$ transition moment calculation with the density matrix averaged atomic natural orbital spd basis sets of Pierloot *et al.* [32] .

*****, The ${}^2\Pi(\text{state},2) \rightarrow {}^2\Sigma^+(\text{state},2)$ transition moment calculation for AsCl^+**

```

memory,4,M

file,2,ascl.wfu

zmat,angstrom

As

Cl,As,r(i)
```

endz

basis={ The same basis sets [32] and f functions as used in the MCSCF }

r=[1.4,1.5,1.6,1.7,1.8,1.9,2.0,2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,3.0,3.1,3.2]

do i=1,#r

int;

text,CASSCF, state averaged orbitals for 2PI to 2sig+ states

multi,start,2140.2;orbital,2140.2;natorb,,ci;

wf,49,1,1;state,2;

wf,49,2,1;state,2;wf,49,3,1;state,2;maxiter,30;

ci,wf,49,1,1;state,2;orbital,2140.2;natorb;maxiter,40;save,8000.2;

ci,wf,49,2,1;state,2;orbital,2140.2;natorb;maxiter,40;save,7000.2;

ci,trans,7000.2,8000.2;

enddo

As in the case of NF^+ and PCl^+ , another transition moment calculation is required.

For the ${}^4\Pi(\text{state},2) \rightarrow {}^4\Sigma^-(\text{state},3)$ transition moments the wavefunctions defined on the WF cards are **wf,31,2,3;wf,31,3,3;** and **wf,31,4,3;** for the ${}^4\Pi(\text{state},2)$ state and for the ${}^4\Sigma^-(\text{state},3)$ state, respectively. By the same method as used in the previous two sections the ${}^4\Pi(\text{state},2) \rightarrow {}^4\Sigma^-(\text{state},3)$ transition moments have been calculated using the same basis sets as above. The results of both transition moment calculations will be shown in Chapter 4 (Results and discussion for AsCl^+).

3.4.11.4 The input file for BBr^+

As in the case of AsCl^+ , three input files are given as follows.

A) The input file for the $^2\Sigma^+$ state using effective core potentials (ECP)

with the vqz basis sets.

*****, BBr^+ excited states for the $^2\Sigma^+$ state in the CI calculation**

file,2,bbrplus.wfu

zmat,angstrom

br

b,br,r(i)

endz

r=[1.4,1.5,1.6,1.7,1.8,1.9,2.0,2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,3.0,3.1,3.2,3.5,4.0,4.5
,5.0]

do i=1,#r

int;

ecp,1,ecp28mwb;

sp,1,ECP28mwb;c;

d,1,0.2;

spd,2,vqz;c

multi,start,2140.2;orbital,2140.2;natorb,,ci;wf,1 1,1,1;state,6;maxiter,30;

ci;maxiter,40;wf,1 1,1,1;state,6;

enddo

For the other five states, the wavefunctions are defined on the WF cards as in the MCSCF calculations. As usual, the calculations have been performed for the six states using the VDZ and VTZ basis sets by the same method as above. All energy values and graphs using the VDZ, VTZ and VQZ basis sets will be presented in the APPENDIX B.

B) The CI input file for the $^2\Sigma^+$ state using the density matrix averaged atomic natural orbital spd basis sets of Pierloot *et al* [32].

*****, The CI calculation for the BBr⁺ excited states**

memory,4,M

file,2,bbr.wfu

zmat,angstrom

B

Br,B,r(i)

endz

basis={The same basis sets [32] and f functions as used in the MCSCF }

r=[1.4,1.5,1.6,1.7,1.8,1.9,2.0,2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,3.0,3.1,3.2,3.5,4.0,4.5
,5.0]

do i=1,#r

int;

multi,start,2140.2;orbital,2140.2;wf,39,1,1;state,6;natorb,,ci;maxiter,25;

ci;wf,39,1,1;state,6;maxiter,40;option,nstati=7;

enddo

The same options on the WF cards are required as used in the MCSCF for the five other states using the basis sets [32]. All the energy values calculated and graphs produced from these jobs will be shown in Chapter 4 (Results and discussion for BBr^+).

C) The input file for the $^2\Pi(5\text{states}) \rightarrow ^2\Sigma^+(6\text{states})$ transition moments is represented with the same basis sets [32] above.

*****, $\text{BBr}^+ \ ^2\Pi(5\text{states}) \rightarrow ^2\Sigma^+(6\text{states})$ transition moments**

memory,4,M

file,2,bbr.wfu

zmat,angstrom

B

Br,B,r(i)

endz

basis={The same basis sets [32] and f functions as used in the MCSCF }

r=[1.4,1.6,1.8,2.0,2.2,2.4,2.6,2.8,3.0]

do i=1,#r

int;

text,CASSCF, state averaged orbitals for 2Π to 2sig^+ states

multi,start,2140.2;orbital,2140.2;natorb,,ci;

wf,39,1,1;state,6;

wf,39,2,1;state,5;wf,39,3,1;state,5;maxiter,30;

```
ci,wf,39,1,1;state,6;orbital,2140.2;natorb;maxiter,40;save,8000.2;
```

```
ci,wf,39,2,1;state,5;orbital,2140.2;natorb;maxiter,40;save,7000.2;
```

```
ci,trans,7000.2,8000.2;
```

```
enddo
```

```
---
```

Unlike NF^+ , PCl^+ and AsCl^+ , no transition moments for the quartet states have been calculated. Transition moments have been calculated for the doublet states only. The transition moments will be given in Chapter 4 (Results and discussion for BBr^+).

3.4.11.5 The input file for HC + NO

There are two input files available, namely for the linear structure and for the bent structure.

A) The input file for the $^1\Sigma^+$ state using the VDZ basis sets is given for the linear geometry

***, The CI calculation for HC + NO 1-Sigma-Plus

```
memory,4,M
```

```
file,2,hcno.wfu
```

```
zmat,angstrom
```

```
h
```

```
c,h,rch
```

```
n,c,rcn(i),h,180
```

```
o,n,rno,c,180
```



```

endz

basis=vdz

rch=1.058

rcn=[1.25,1.5,1.75,2.0,2.5,3.0,3.5,4.0,4.5,5.0]

rno=1.198

do i=1,#rcn

int;

text,CASSCF, state averaged orbitals for 1SIG+ states

multi,occ,10,3,3;closed,5,0,0;start,2140.2;orbital,2140.2;natorb,,ci;

wf,22,1,0;state,2;maxiter,25;

ci,occ,10,3,3;core,6,0,0;wf,22,1,0;state,2;maxiter,25;

enddo

---
```

For the these other states considered, the wavefunctions are specified on the WF cards as in the MCSCF, namely $^1\Sigma^-$ (wf,22,4,0) , $^3\Sigma^+$ (wf,22,1,2) and $^3\Sigma^-$ (wf,22,4,2). All the energy values and graphs will be given in Chapter 4 (Results and discussion for HC + NO).

B) The input file for the $^1A'$ state using the VDZ basis sets is with the bent geometry.

*****, The CI calculation for HC + NO $^1A'$ state**

```

memory,6,M

file,2,hcno.wfu

zmat,z,angstrom
```

```

h
c,h,rch
n,c,rcn,h,theta(i)
o,n,rno,c,180
endz
basis=vdz
rch=1.058
rcn=1.750
rno=1.198
theta=[180,170,160,150,140,130,120]
do i=1,#theta
int;
text,CASSCF, state averaged orbitals for 1A' states
multi,occ,13,3;closed,5,0;start,2140.2;orbital,2140.2;natorb,,ci;
wf,22,1,0;state,2;maxiter,25;
ci;occ,13,3;core,6,0;wf,22,1,0;state,2;maxiter,25;
enddo
---
```

Here also, for calculations for A'' or triplet states the appropriate changes have to be made to the WF cards as in the MCSCF calculations. However, due to lack of time these calculations are left for further work. Thus, the results and discussion section in Chapter 4 for HC + NO will show energy values and graphs only for the $^1A'$ states.

4. Results and Discussion

Our work is divided into two categories, namely potential energy curves for diatomic molecular ions and potential surfaces for $\text{HC} + \text{NO}$ as described in the Introduction.

4.1 Potential energy curves for diatomic molecular ions

Our calculations treat the low-lying electronic states of the molecular ions NF^+ , PCl^+ , AsCl^+ and BBr^+ correlating with the lowest dissociation asymptotes, namely $\text{N}^+(^3\text{P}) + \text{F}(^2\text{P})$, $\text{P}^+(^3\text{P}) + \text{Cl}(^2\text{P})$, $\text{As}^+(^3\text{P}) + \text{Cl}(^2\text{P})$, $\text{B}^+(^1\text{S}) + \text{Br}(^2\text{P})$ and $\text{B}(^2\text{P}) + \text{Br}^+(^3\text{P})$.

From the Wigner-Witmer correlation rules the above dissociation asymptotes correlate with the following states

For NF^+ , PCl^+ and AsCl^+ $^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Pi(2)$, $^4\Delta$.

For BBr^+ $^2\Sigma^+$, $^2\Pi$ from $\text{B}^+(^1\text{S}) + \text{Br}(^2\text{P})$ and $^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Pi(2)$, $^4\Delta$ from $\text{B}(^2\text{P}) + \text{Br}^+(^3\text{P})$.

CASSCF and CI calculations have been performed using the correlation-consistent valence quadruple-zeta basis sets for NF^+ , PCl^+ and averaged atomic natural orbital (ANO) basis sets for AsCl^+ , BBr^+ .

All energy values and potential energy curves obtained from the calculations above will be given in sections 4.1.1, 4.1.2, 4.1.3 and 4.1.4 for NF^+ , PCl^+ , AsCl^+ and BBr^+ respectively. The results of calculations with the VDZ, VTZ basis sets for NF^+ , PCl^+ , and with the basis sets VDZ, VTZ and VQZ for AsCl^+ and BBr^+ using effective core potentials will be reported in APPENDIX B. One of our aims in the calculations for the diatomic molecular ions is to derive spectroscopic constants for the bound states obtained as mentioned in the Introduction.

To calculate spectroscopic constants we have used the LEVEL program by LeRoy.

The program LEVEL can calculate solutions of the nuclear Schrödinger equation for bound and quasibound levels for any smooth one-dimensional or radial potential. The aim of this program is to obtain the discrete eigenvalues and eigenfunctions of the radial or (effective) one-dimensional nuclear Schrödinger equation as follows

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \Psi_{v,J}(R)}{dR^2} + V_J(R) \Psi_{v,J}(R) = E_{v,J} \Psi_{v,J}(R) \quad (4.1)$$

where μ represents the effective or reduced mass, J the rotational quantum number, and the effective one-dimensional potential $V_J(R)$ accounts for the sum of the rotationless (electronic) potential plus a centrifugal term. For the usual problem of a diatomic molecule rotating in three dimensions, this centrifugal potential has the form $[J(J+1) - \Omega^2] \hbar^2 / 2\mu R^2$ where Ω ($=$ IOMEG in the input to the program) defines the projection of the electronic angular momentum on to the internuclear axis.

The solution of Schrödinger equation shown above is crucial to the determination of the eigenvalues $E_{v,J}$ and eigenfunctions $\Psi_{v,J}(R)$ of the potential $V_J(R)$. The accuracy of these eigenfunctions and eigenvalues largely depends on the size of the (fixed) radial mesh RH used in the numeral integration of Schrödinger equation above. For potentials that are not too steep or too sharply curved, suitable accuracy is generally provided with an RH value which produces a minimum of 15 to 30 mesh points between adjacent wavefunction nodes in the classically allowed region. A suitable mesh size may thus be computed with the expression

$$RH = \pi / NH [(\mu / 16.8576314) \max\{E - V(R)\}_{rsp}]^{1/2} \quad (4.2)$$

where NH represents the selected minimum number of points per wavefunction node (say 20), the quantity $\max\{E - V(R)\}$ is expressed as the maximum of the local kinetic energy (in cm^{-1}) for the levels under consideration (usually it is \leq the well depth). For the bound states, rotation-vibrational energy levels were obtained by the numerical solution of the nuclear Schrödinger equation with the program of LeRoy [153] using the calculated potential energy curves. Spectroscopic constants were generated from the energy levels as follows. The vibration constants ω_e and $\omega_e x_e$ were derived by fitting the energies $E(\nu, J = 0)$ to the expression:

$$E(\nu) = \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2 \quad (4.3)$$

The rotational constant B_ν was generated by fitting rotational levels $J = 0$ to $J = 6$ for each vibration state of $\nu = 0$ to $\nu = 2$ to the expression

$$E_\nu(J) = B_\nu J(J + 1) - D_\nu J^2(J + 1)^2 \quad (4.4)$$

and eventually B_e and the vibration-rotation interaction constant α_e were calculated by fitting the B_ν values to

$$B_\nu = B_e - \alpha_e(\nu + 1/2) \quad (4.5)$$

For each of NF^+ , PCl^+ , AsCl^+ , only four bound states, namely $\text{X}^2\Pi$, $\text{A}^2\Pi$, $1^4\Sigma^-$ and $1^4\Pi$ are obtained whereas for BBr^+ there are many more bound states, namely $\text{X}^2\Sigma^+$, $2^2\Sigma^+$, $1^2\Pi$, $2^2\Pi$, $1^2\Delta$, $1^2\Sigma^-$, $4^+\Sigma$, $4^+\Delta$ and $1^4\Sigma^-$. Spectroscopic constants are calculated for all the bound states by the above LeRoy program. However, for BBr^+ our values disagree with experimental parameters in the literature of a $^2\Pi_r \rightarrow \text{X}^2\Sigma^+$ system. Thus, it is suggested that the reinvestigation of the spectroscopy of BBr^+ would be worthwhile.

4.1.1 The results for NF^+

As mentioned earlier in chapter 3, these calculations have been made using the MOLPRO suite of programs [156] and we have used the correlation-consistent valence quadruple-zeta (cc: vqz) basis sets from Dunning [157] and Woon and Dunning [158]. The VQZ basis sets used are composed of 12s6p basis sets contracted to 5s4p functions, and three sets of d functions, two sets of f functions and one set of g functions generating a basis set of 110 contracted Gaussian functions. For each spin and symmetry species the wavefunctions for the following CI calculations were derived from the orbitals obtained in state averaged CASSCF calculations [146, 147] where state averaging was carried out over the states of interest. The active orbitals comprised the valence orbitals $3\sigma - 6\sigma$, 1π and 2π . Multi-reference CI calculations, with the sets of reference configurations generated in the CASSCF calculations, were made with the internally contracted CI method of Knowles and Werner [150,151]. Table 4.1 shows details of configuration interaction calculations with the sizes of the reference spaces (A), the numbers of contracted (B) and uncontracted (C) configurations and the numbers of roots calculated (D).

Table 4.1 Details of configuration interaction calculations

State	A	B	C	D
$^2\Sigma^+$	264	481368	7613384	5
$^2\Pi$	252	232860	7016380	2
$^2\Sigma^-$	240	480352	6410288	5
$^4\Sigma^+$	108	461380	6082652	5
$^4\Pi$	126	213854	5983882	2
$^4\Sigma^-$	144	296980	5682628	3

The energies obtained in the CI calculations and the calculated potential energy curves are given in tables and figures 4.1.1 to 4.1.6 for the $^2\Pi$, $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^-$, $^4\Sigma^+$ and $^4\Pi$ states, respectively. Also, the dominant configurations for the six states are described, in turn, in subsections 4.1.1.1.A to 4.1.1.6.A and these show how the configurations change at avoided crossings. The orbitals 3σ and 4σ correspond predominantly to fluorine and nitrogen $2s$ orbitals, respectively. In the region of $r = 1.185\text{\AA}$ the orbitals 5σ and 6σ are bonding and antibonding combinations of the $2p_\sigma$ orbitals on fluorine and nitrogen, and the orbitals 1π and 2π represent bonding and antibonding combinations of $2p_\pi$ orbitals on the two atoms with the major contribution to 1π for fluorine and to 2π for nitrogen.

For large r the orbitals 5σ and 6σ correlate with $2p_\sigma$ orbitals on fluorine and nitrogen respectively and also, the orbitals 1π and 2π correlate with p_π orbitals on fluorine and nitrogen respectively.

4.1.1.1 The CI calculations for the $^2\Pi$ states of NF^+ with the VQZ basis sets

Table 4.1.1 shows the total energy values generated as the bond length is varied. Figure 4.1.1 presents the potential energy curves produced from table 4.1.1 provided above. Table 4.1.1.1.A gives the dominant configurations in the CI wavefunctions at each bond length for the $^2\Pi$ state.

Table 4.1.1.1.A Dominant configurations for the $^2\Pi$ state

State	Configuration	Bond length
$1^2\Pi$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1$	$r \leq 1.8 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3 2\pi^2$	$r \geq 1.9 \text{ \AA}$
$2^2\Pi$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3 2\pi^2$	$r \leq 1.9 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 6\sigma^1 1\pi^4 2\pi^1$	$r \geq 2.0 \text{ \AA}$

As shown in figure 4.1.1, two potential curves for the two roots are produced. The minima in the curves give the equilibrium bond lengths R_e . The depth of the potential well represents the dissociation energy relative to the equilibrium configuration. Root1($1^2\Pi$) has a reasonable amount of binding and Root2($2^2\Pi$) is bound. Thus, for both states we have calculated the spectroscopic constants and also the $1^2\Pi$ state has been investigated experimentally [7,57]. The theoretical and experimental spectroscopic parameters are given in table 4.1.1.1.B and they are compared as follows.

Table 4.1.1.1.B Spectroscopic constants for the $^2\Pi$ state

CONSTS	EXPT.[7]	THEO.[57]	ROOT1($1^2\Pi$)	ROOT2($2^2\Pi$)
ω_e/cm^{-1}	1520 ± 40	1499	1561.38	560.97
$\omega_e x_e/\text{cm}^{-1}$	10 ± 6		13.80	16.27
B_0/cm^{-1}			1.4810	0.7186
B_1/cm^{-1}			1.4634	0.7006
B_2/cm^{-1}			1.4456	0.6803
B_e/cm^{-1}			1.4899	0.7285
α_e/cm^{-1}			0.0177	0.0191
$R_e/\text{\AA}$	1.180	1.182	1.185	1.695

For the comparison of our values with experimental parameters [7], the computed vibration constant (ω_e) and bond length (R_e) are in good agreement with data from reference [7] with the errors of 2.7 % and 0.42 % and there is reasonable agreement

between the calculated value (13.80 cm^{-1}) and experimental value ($10 \pm 6 \text{ cm}^{-1}$) for the anharmonicity constant ($\omega_e x_e$).

Compared with the theoretical values from reference [57], the calculated constants ω_e and R_e differ by 4.1% and 0.25%. However, the spectroscopic constants of the $2^2\Pi$ state have not been obtained experimentally. Thus, the theoretical data of root2 can be used for the prediction of experimental values.

4.1.1.2 The CI calculations for the $^2\Sigma^+$ states of NF^+ with the VQZ basis sets

In initial calculations for 2 states, mixing with other states caused problems. Thus, to obtain reasonable values and to avoid convergence problems we have considered 5 states rather than the numbers of states defined in figure 1.

Table 4.1.2 shows the energies of the five roots at each bond length and we consider the first two roots. Figure 4.1.2 shows the two corresponding potential energy curves.

As earlier described in the Introduction, when a CI calculation of the $^2\Sigma^+$ state is performed under C_{2v} symmetry, both $^2\Sigma^+$ and $^2\Delta$ states are obtained. As shown in figure 1 (Chapter 1) a $^2\Delta$ state arises from the combination of $\text{F}(^2\text{P}) + \text{N}^+(^3\text{P})$. For each of the roots obtained we have examined the wavefunctions and labelled the states as appropriate. Root1 is a $^2\Sigma^+$ state and root2 is a $^2\Delta$ state. However, in the CI calculations located in APPENDIX B, not only for NF^+ using VDZ and VTZ basis sets, but also for PCl^+ using VDZ and VTZ basis sets, for AsCl^+ using VDZ, VTZ and

VQZ basis sets and for BBr^+ using VDZ, VTZ and VQZ basis sets we have not distinguished the Σ^+ (or Σ^-) and Δ wavefunctions because these were preliminary calculations with smaller basis sets than those used in this chapter. Use of the more extensive basis sets yields accurate spectroscopic constants compared with experimental parameters.

Table 4.1.1.2.A presents the dominant configurations for the $^2\Sigma^+$ state as the bond length is varied.

Table 4.1.1.2.A Dominant configurations for the $^2\Sigma^+$ state

State	Configuration	Bond length
$^2\Sigma^+$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^2$	$r \leq 1.2 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^1 1\pi^4$	$1.3 \leq r \leq 1.7 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^1 1\pi^3 2\pi^1$	$r \geq 1.8 \text{ \AA}$
$^2\Delta$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^2$	$r \leq 1.7 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^1 1\pi^3 2\pi^1$	$r \geq 1.8 \text{ \AA}$

As shown in figure 4.1.2, state 1 has a very shallow minimum whereas state 2 is repulsive. There are no bound states in this case. Thus, spectroscopic constants have not been calculated. Spectroscopic parameters for the $^2\Sigma^+$ and $^2\Delta$ states have not been obtained experimentally, either.

4.1.1.3 The CI calculations for the $^2\Sigma^-$ states of NF^+ with the VQZ basis sets

To avoid convergence problems we have calculated 5 states rather than the 3 states expected from the combination of $\text{F}(^2\text{P}) + \text{N}^+(^3\text{P})$ shown in figure 1. Thus, table 4.1.3 gives the energies of the five roots at each bond length and the three lowest roots have been selected. Figure 4.1.3 shows the corresponding three potential energy

curves for the first three roots. As in the $^2\Sigma^+$ case, the $^2\Sigma^-$ calculation gives both $^2\Sigma^-$ and $^2\Delta$ wavefunctions under C_{2v} symmetry. The wavefunctions have been examined and assigned to $^2\Sigma^-$ and $^2\Delta$ accordingly. Root1 and Root3 are $^2\Sigma^-$ states and root2 is a $^2\Delta$ state. Table 4.1.1.3.A gives the dominant configurations for the $^2\Sigma^-$ states as the bond length changes.

Table 4.1.1.3.A Dominant configurations for the $^2\Sigma^-$ state

State	Configuration	Bond length
$1^2\Sigma^-$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^2$	
$2^2\Sigma^-$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^3$	$r \leq 1.3 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^1 1\pi^3 2\pi^1$	$r \geq 1.4 \text{ \AA}$

For the $^2\Delta$ state the dominant configurations are given in the previous section. All three roots are repulsive as shown in figure 4.1.3. Thus, no spectroscopic constants have been calculated for the $^2\Sigma^-$ state. In addition, no experimental data are available for these three states.

4.1.1.4 The CI calculations for the $^4\Sigma^-$ states of NF^+ with the VQZ basis sets

Table 4.1.4 presents the energies for the three roots at the various bond lengths and figure 4.1.4 shows the corresponding three potential energy curves. The $^4\Sigma^-$ calculation produces both $^4\Sigma^-$ and $^4\Delta$ wavefunctions under C_{2v} symmetry as in the $^2\Sigma^-$ case discussed in the previous section. The wavefunctions have been examined and assigned to $^4\Sigma^-$ and $^4\Delta$ as appropriate.

The root1 and root3 are $^4\Sigma^-$ states and root2 is a $^4\Delta$ state. Table 4.1.1.4.A gives the dominant configurations for the $^4\Sigma^-$ states as the bond length is changed.

Table 4.1.1.4.A Dominant configurations for the $^4\Sigma^-$ state

State	Configuration	Bond length
$1^4\Sigma^-$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^2$	$r \leq 2.1 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^1 1\pi^3 2\pi^1$	$r \geq 2.2 \text{ \AA}$
$2^4\Sigma^-$	$\cdots 3\sigma^2 4\sigma^1 5\sigma^2 1\pi^4 2\pi^2$	$r \leq 1.3 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^1 1\pi^3 2\pi^1$	$1.4 \leq r \leq 2.1 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^2$	$r \geq 2.2 \text{ \AA}$
$^4\Delta$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^3$	$r \leq 1.2 \text{ \AA}$
	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^1 1\pi^3 2\pi^1$	$r \geq 1.3 \text{ \AA}$

State 1 has a reasonable amount of binding. State 2 has a very shallow minimum and state 3 is repulsive. Therefore, only the spectroscopic constants for the $1^4\Sigma^-$ state have been calculated and are given in table 4.1.1.4.B.

Table 4.1.1.4.B Spectroscopic constants for the $1^4\Sigma^-$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$1^4\Sigma^-$	1018.40	24.50	1.2294	1.1984	1.1671	1.2450	0.0311	1.295

However, there are no experimental parameters for the $^4\Sigma^-$ state. Thus, the spectroscopic constants calculated for the root1 can be predictive of experimental data.

4.1.1.5 The CI calculations for the $^4\Sigma^+$ states of NF^+ with the VQZ basis sets

Here, for the $^4\Sigma^+$ calculation we met the same problems as the $^2\Sigma^+$ and $^2\Sigma^-$ calculations.

To obtain a satisfactory description of the lowest states we have calculated 5 states rather than 2 states which correlate with the combination of $\text{F}(^2\text{P}) + \text{N}^+(^3\text{P})$ in figure 1.

Table 4.1.5 gives the energy values for the five roots at each bond length and we have chosen the first two lowest roots. Figure 4.1.5 shows the two corresponding potential energy curves for the two roots selected.

As in the $^4\Sigma^-$ case, the $^4\Sigma^+$ calculation gives both $^4\Sigma^+$ and $^4\Delta$ wavefunctions.

The wavefunctions have been analysed and labelled $^4\Sigma^+$ and $^4\Delta$ as appropriate.

Table 4.1.1.5.A gives the dominant configurations for the $^4\Sigma^+$ state as the bond length is varied.

Table 4.1.1.5.A Dominant configurations for the $^4\Sigma^+$ state

State	Configuration	Bond length
$^4\Sigma^+$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^1 1\pi^3 2\pi^1$	

For the $^4\Delta$ wavefunction we have the same dominant configurations as for the $^4\Sigma^-$ state in the previous section. Root1 and root2 are $^4\Sigma^+$ and $^4\Delta$ states respectively. Both states 1 and 2 have very shallow minima. Therefore, no spectroscopic constants have been calculated for both states. Furthermore, experimental parameters for the $^4\Sigma^+$ state have not been determined.

4.1.1.6 The CI calculations for the $^4\Pi$ states of NF^+ with the VQZ basis sets

Table 4.1.6 contains the energies of the two roots at each bond length and figure 4.1.6 shows the two corresponding potential energy curves. Table 4.1.1.6.A presents the dominant configurations for the $^4\Pi$ states as the bond length is varied.

Table 4.1.1.6.A Dominant configurations for the ${}^4\Pi$ state

State	Configuration	Bond length
$1^4\Pi$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3 2\pi^2$	
$2^4\Pi$	$\cdots 3\sigma^2 4\sigma^2 5\sigma^1 6\sigma^1 1\pi^4 2\pi^1$	

As shown in figure 4.1.6 the root1 is reasonably bound and the root2 is repulsive.

Thus, spectroscopic constants have been calculated for the $1^4\Pi$ state and given in table 4.1.1.6.B.

Table 4.1.1.6.B Spectroscopic constants of the root1 for the ${}^4\Pi$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$1^4\Pi$	618.54	8.61	0.7496	0.7370	0.7244	0.7559	0.0126	1.665

On the other hand, experimental values for the ${}^4\Pi$ state have not been obtained.

Therefore, calculated values can be used for the prediction of experimental parameters.

4.1.1.7 General discussion for NF^+

Figures 4.1.9 and 4.1.10 show the potential energy curves for the doublet and quartet states respectively. From the figures 4.1.9 and 4.1.10 it can be seen that there are relatively few bound states, namely $X^2\Pi$, $A^2\Pi$, $1^4\Sigma^-$ and ${}^4\Pi$. Thus, it is not unexpected that optical spectra have not been observed for this system. The lowest root for the ${}^2\Pi$ state calculation is the ground state, $X^2\Pi$, which has an equilibrium bond length of 1.185 Å and the second root is the $A^2\Pi$ state which has a very shallow minimum at the bond length of 1.695 Å. In contrast, the theoretical potential-energy curves we have calculated for the PF^+ molecular ion [1] show that the lowest ${}^2\Sigma^+$ state has a shallow minimum and the $2^2\Pi$ state is repulsive. None of the other doublet

states for NF^+ are bound. For NF^+ the dissociation asymptote $\text{F}(^2\text{P}) + \text{N}^+(^1\text{D})$ is 1.90 eV higher. Even though we have not considered the calculation of the potential-energy curves for all of the states correlating with the dissociation asymptote mentioned above we find that the humps in the curves for the $^2\Sigma^+$, $^2\Delta$ and $2^2\Sigma^-$ states at $r = 1.4 \text{ \AA}$, 1.7 \AA and 1.3 \AA respectively arise from avoided intersections with states correlating with the dissociation asymptote $\text{F}(^2\text{P}) + \text{N}^+(^1\text{D})$. For the quartet states there are only two bound states, namely the lower $^4\Pi$ and $^4\Sigma^-$ states. However, the potential wells of both states are shallow. The equilibrium bond lengths of the two states mentioned above are very different. Thus, it would be expected that the Franck-Condon factors would be very unfavourable. Table 4.1.1.7.A shows the calculated energies for the six states we have considered relative to the ground state $\text{X}^2\Pi$ at the equilibrium bond length of $r_e = 1.185 \text{ \AA}$, the energies for different bound states at their equilibrium bond lengths, T_e values, dipole moments, and spectroscopic constants. As mentioned earlier in subsection 4.1.1.1, for the $\text{X}^2\Pi$ state theoretical equilibrium bond length is in good agreement with the experimental data of Dyke *et al.* [7] but in less good agreement with the theoretical value of Bettendorf and Peyerimhoff [57]. However, in their calculation they have used natural orbitals for the neutral NF molecule rather than orbitals computed for NF^+ . Dipole moments and dipole moment functions for the bound states, namely $\text{X}^2\Pi$, $\text{A}^2\Pi$, $1^4\Sigma^-$ and $1^4\Pi$, are presented in table 4.1.7 and figure 4.1.7 and also the electronic transition moments and the transition moment functions are given in table 4.1.8 and figure 4.1.8. For an ion the dipole moment depends on the origin chosen. Dipole moments have been calculated with respect to the centre of mass and in the direction NF. Since all the

bound states mentioned above dissociate to $N^+ + F$, as the internuclear distance is increased all of the dipole moment functions should approach the same linear function and this is the case in figure 4.1.8. The $A^2\Pi$ state supports at least 9 vibrational levels and in the region of the equilibrium bond length of the $A^2\Pi$ state the transition moment for the $A^2\Pi \rightarrow X^2\Pi$ transition has a reasonable value. Thus, it would be expected that this transition might be observed in emission spectroscopy. The spectroscopic parameters we have calculated should be useful as a first approximations to those of the $A^2\Pi$ state.

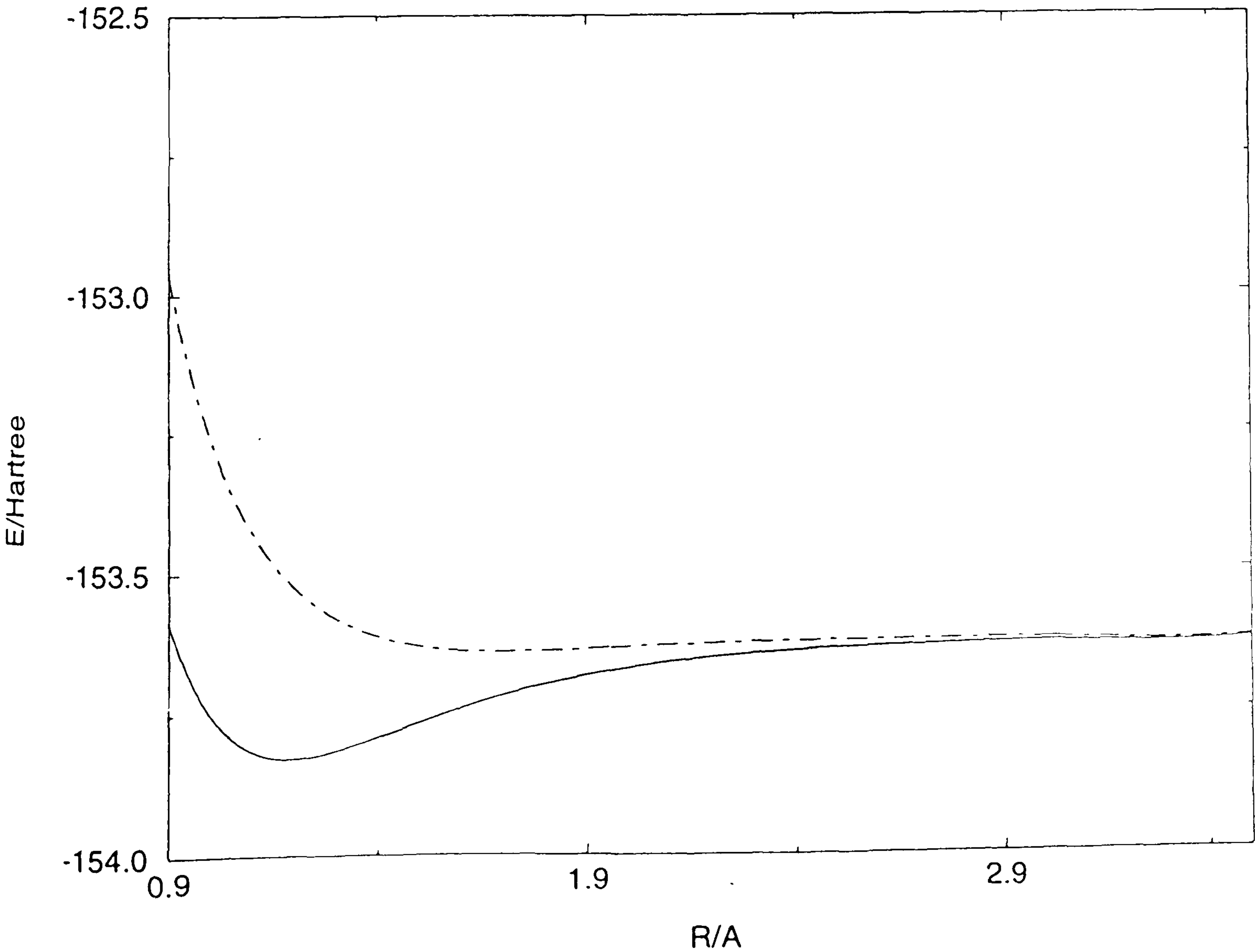
4.1.1 The CI results for the $^2\Pi$ states of NF^+ with the VQZ basis sets

Table 4.1.1 Theoretical energy values

R/Å	ROOT1	ROOT2
0.85	-153.430820	-152.733294
0.90	-153.583096	-152.961493
1.00	-153.751567	-153.259393
1.10	-153.815202	-153.426624
1.20	-153.826825	-153.522375
1.30	-153.813924	-153.578224
1.40	-153.790670	-153.610701
1.50	-153.764400	-153.628552
1.60	-153.738931	-153.636776
1.70	-153.716085	-153.638642
1.80	-153.696739	-153.636998
1.90	-153.681092	-153.634083
2.00	-153.668747	-153.631110
2.10	-153.659101	-153.628575
2.20	-153.651586	-153.626592
2.30	-153.645743	-153.625112
2.40	-153.641212	-153.624040
2.50	-153.637702	-153.623286
2.75	-153.631995	-153.622316
3.00	-153.628895	-153.622063
3.50	-153.626031	-153.622224

E/Hartree

Figure 4.1.1 Calculated potential energy curves



4.1.2 The CI results for the $^2\Sigma^+$ states of NF^+ with the VQZ basis sets

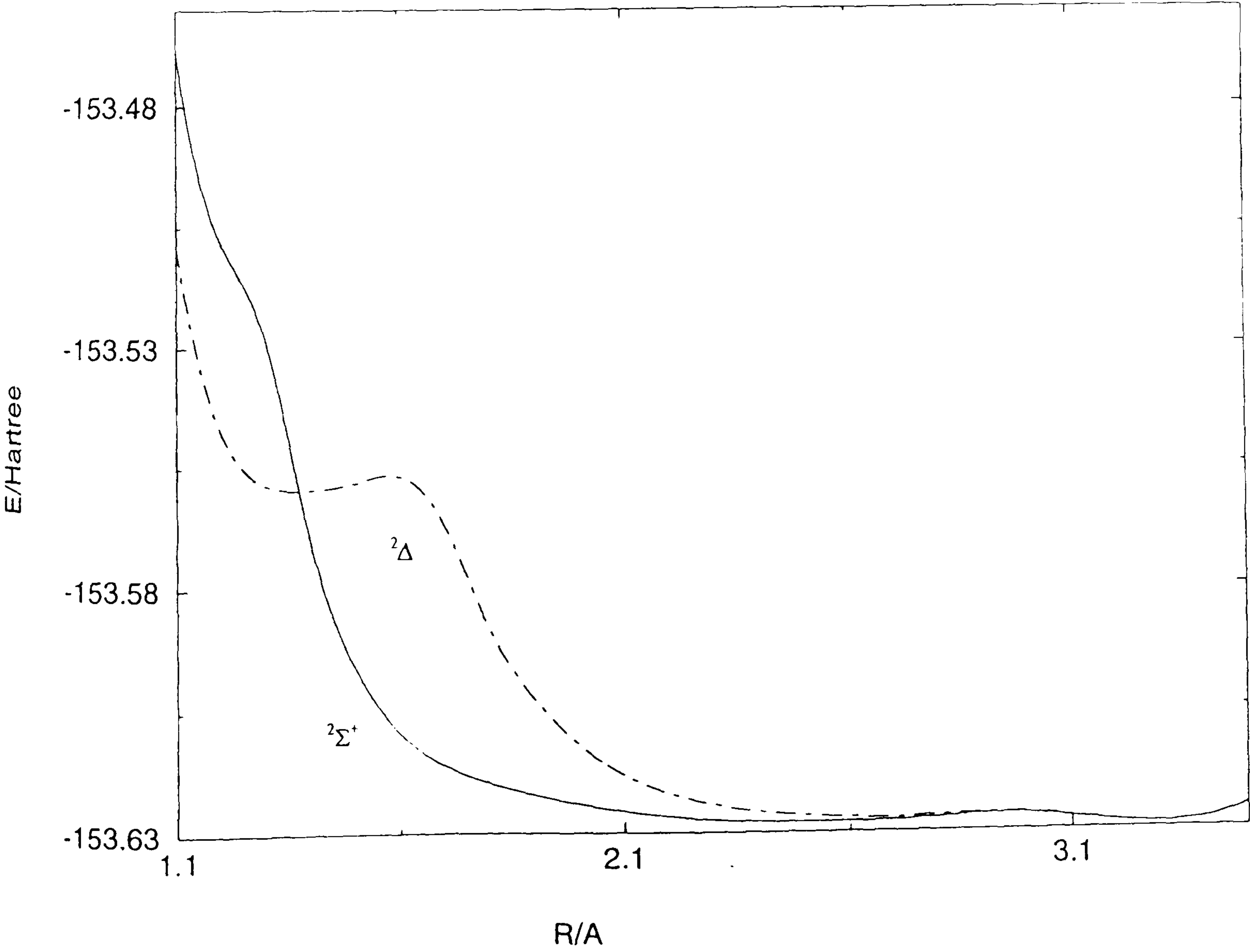
Table 4.1.2 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.1	-153.468483	-153.508570	-153.326009	-153.185719	-153.150559
1.2	-153.507789	-153.547281	-153.436503	-153.271410	-153.240594
1.3	-153.528016	-153.558347	-153.508203	-153.328474	-153.298695
1.4	-153.569860	-153.559305	-153.515390	-153.415317	-153.390680
1.5	-153.595908	-153.557978	-153.514846	-153.485621	-153.457556
1.6	-153.609469	-153.556616	-153.533496	-153.515853	-153.500379
1.7	-153.616187	-153.566495	-153.554704	-153.529880	-153.516331
1.8	-153.619817	-153.588014	-153.553844	-153.545548	-153.532042
1.9	-153.622249	-153.602377	-153.554045	-153.553438	-153.542720
2.0	-153.624195	-153.611879	-153.558048	-153.553811	-153.548269
2.25	-153.627266	-153.623420	-153.559790	-153.557279	-153.550097
2.5	-153.628071	-153.626754	-153.558703	-153.557831	-153.549878
2.75	-153.627706	-153.627200	-153.557437	-153.557111	-153.549932
3.0	-153.626974	-153.626750	-153.556333	-153.556194	-153.550154
3.5	-153.625622	-153.625554	-153.554772	-153.554755	-153.550674

$^2\Sigma^+$
 $^2\Delta$

E/Hartree

Figure 4.1.2 Calculated potential energy curves



4.1.3 The CI results for the $^2\Sigma^-$ state of NF^+ with the VQZ basis sets

Table 4.1.3 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.1	-153.456004	-153.509464	-153.202217	-153.186561	-153.109456
1.2	-153.515960	-153.547222	-153.290937	-153.271758	-153.183315
1.3	-153.550161	-153.558188	-153.337551	-153.328596	-153.300888
1.4	-153.572342	-153.558839	-153.414763	-153.415439	-153.370879
1.5	-153.587316	-153.557406	-153.485168	-153.485694	-153.439625
1.6	-153.597736	-153.556016	-153.533035	-153.533539	-153.484665
1.7	-153.605036	-153.566469	-153.565250	-153.554227	-153.513440
1.8	-153.610148	-153.587863	-153.586875	-153.553674	-153.531379
1.9	-153.613720	-153.602265	-153.601307	-153.555270	-153.542158
2.0	-153.616278	-153.611766	-153.610781	-153.553091	-153.548659
2.1	-153.618714	-153.618048	-153.616168	-153.555076	-153.553099
2.2	-153.622034	-153.621935	-153.618058	-153.556620	-153.555472
2.3	-153.624306	-153.624507	-153.618958	-153.557463	-153.556680
2.4	-153.625766	-153.625973	-153.619540	-153.557773	-153.557202
2.5	-153.626586	-153.626777	-153.619956	-153.557751	-153.557319
2.75	-153.627088	-153.627226	-153.620643	-153.557049	-153.556811
3.0	-153.626680	-153.626774	-153.621099	-153.556133	-153.555990
3.5	-153.625533	-153.625577	-153.621735	-153.554689	-153.554628

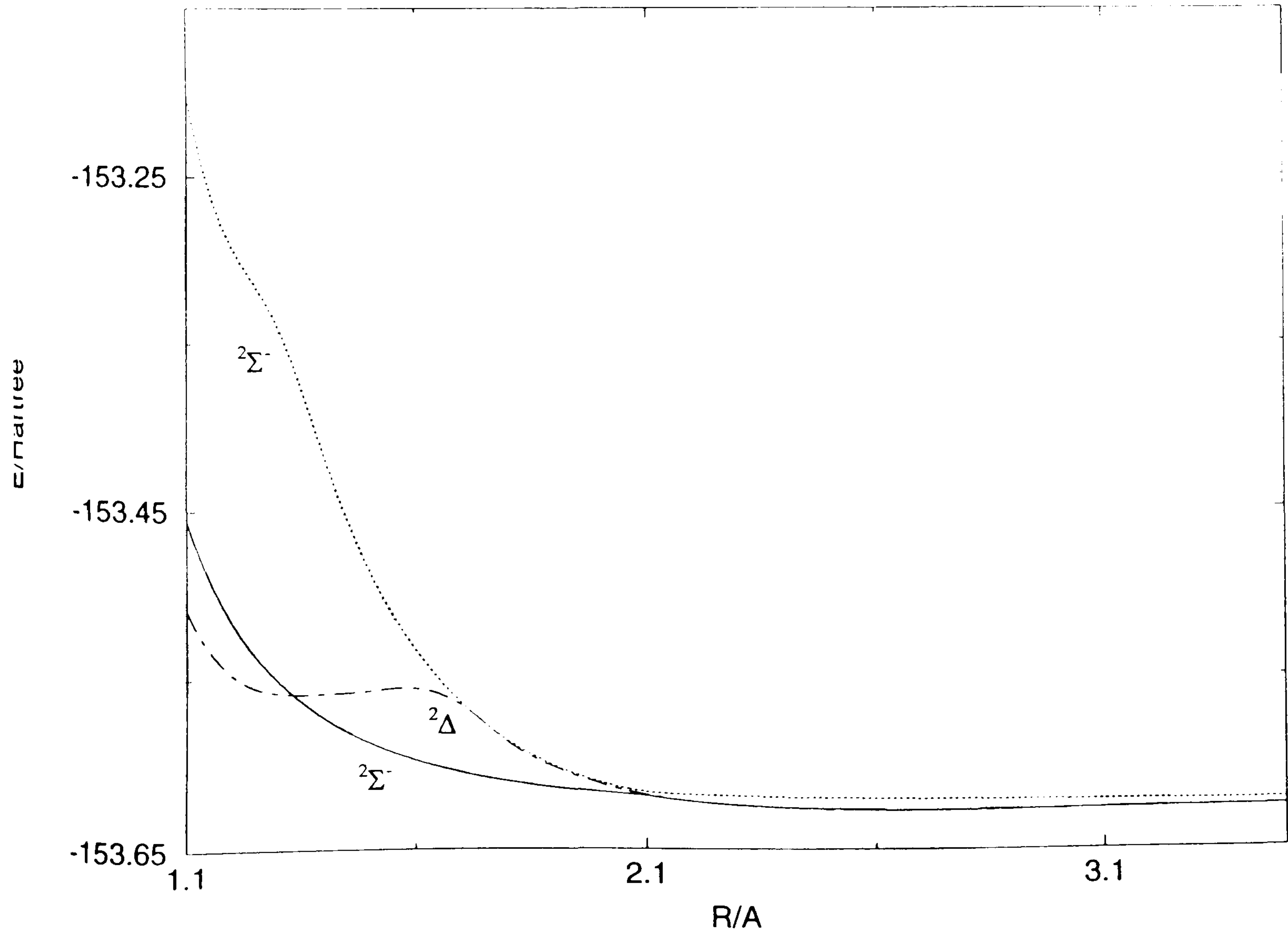
$^2\Sigma^-$

$^2\Delta$

$^2\Sigma^-$

E/Hartree

Figure 4.1.3 Calculated potential energy curves



4.1.4 The CI results for the $^4\Sigma^-$ states of NF^+ with the VQZ basis sets

Table 4.1.4 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.00	-153.524959	-153.002124	-153.123630
1.10	-153.620784	-153.183766	-153.263661
1.20	-153.656580	-153.281239	-153.342526
1.30	-153.663855	-153.350704	-153.389321
1.40	-153.659534	-153.446098	-153.443217
1.50	-153.651612	-153.511916	-153.506821
1.60	-153.643746	-153.555079	-153.550549
1.70	-153.637300	-153.582993	-153.579238
1.75	-153.634706	-153.592924	-153.589526
1.80	-153.632513	-153.600847	-153.597766
1.90	-153.629177	-153.612149	-153.609555
2.00	-153.627021	-153.619205	-153.616832
2.10	-153.626016	-153.623506	-153.620830
2.20	-153.626411	-153.626027	-153.622068
2.30	-153.627405	-153.627299	-153.621967
2.40	-153.628062	-153.627860	-153.621684
2.50	-153.628273	-153.628068	-153.621466
2.75	-153.627861	-153.627713	-153.621289
3.00	-153.627033	-153.626935	-153.621412
3.50	-153.625617	-153.625572	-153.621888

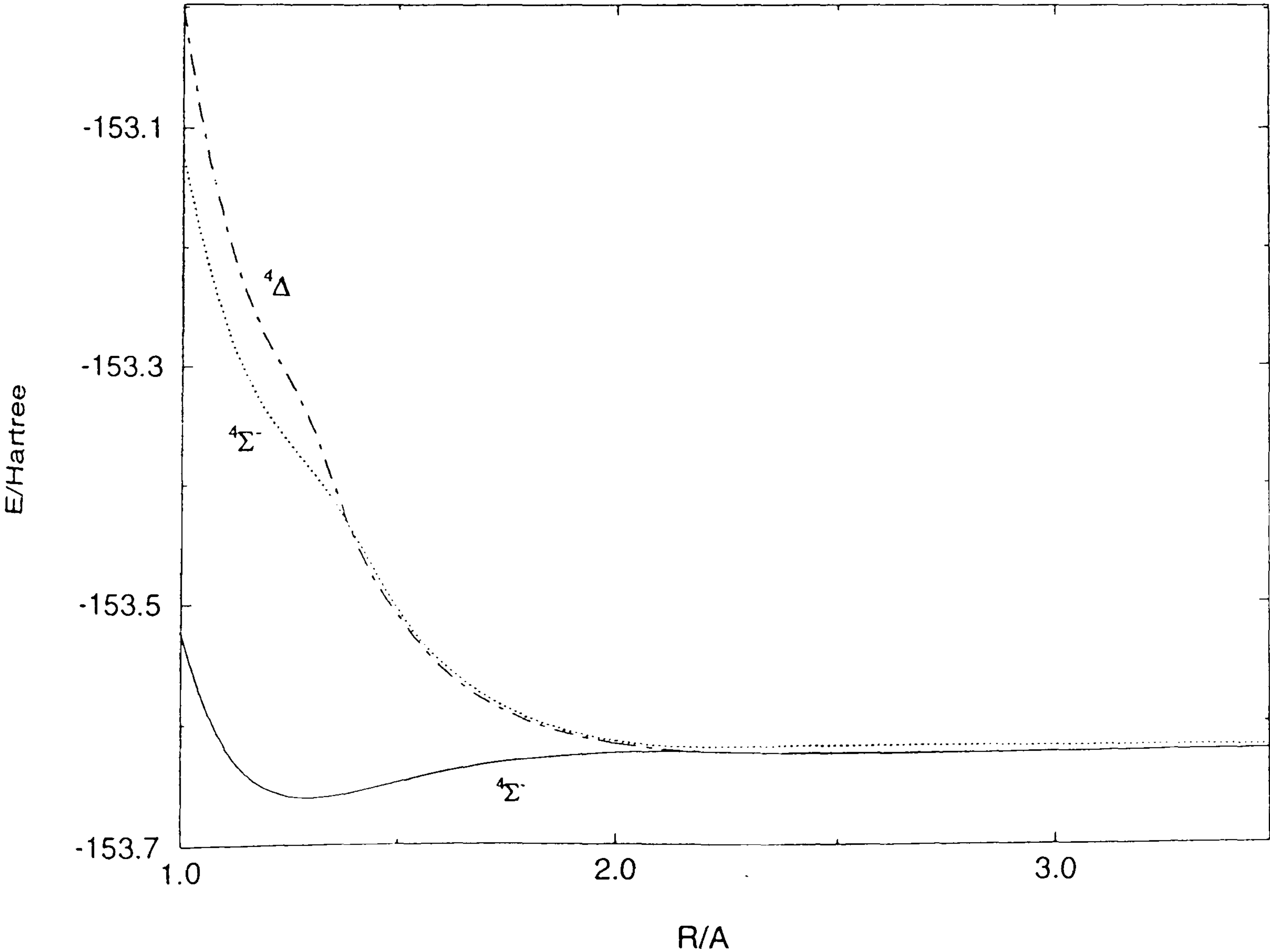
$^4\Sigma^-$

$^4\Delta$

$^4\Sigma^-$

E/Hartree

Figure 4.1.4 Calculated potential energy curves



4.1.5 The CI results for the $^4\Sigma^+$ states of NF^+ with the VQZ basis sets

Table 4.1.5 Theoretical energy values

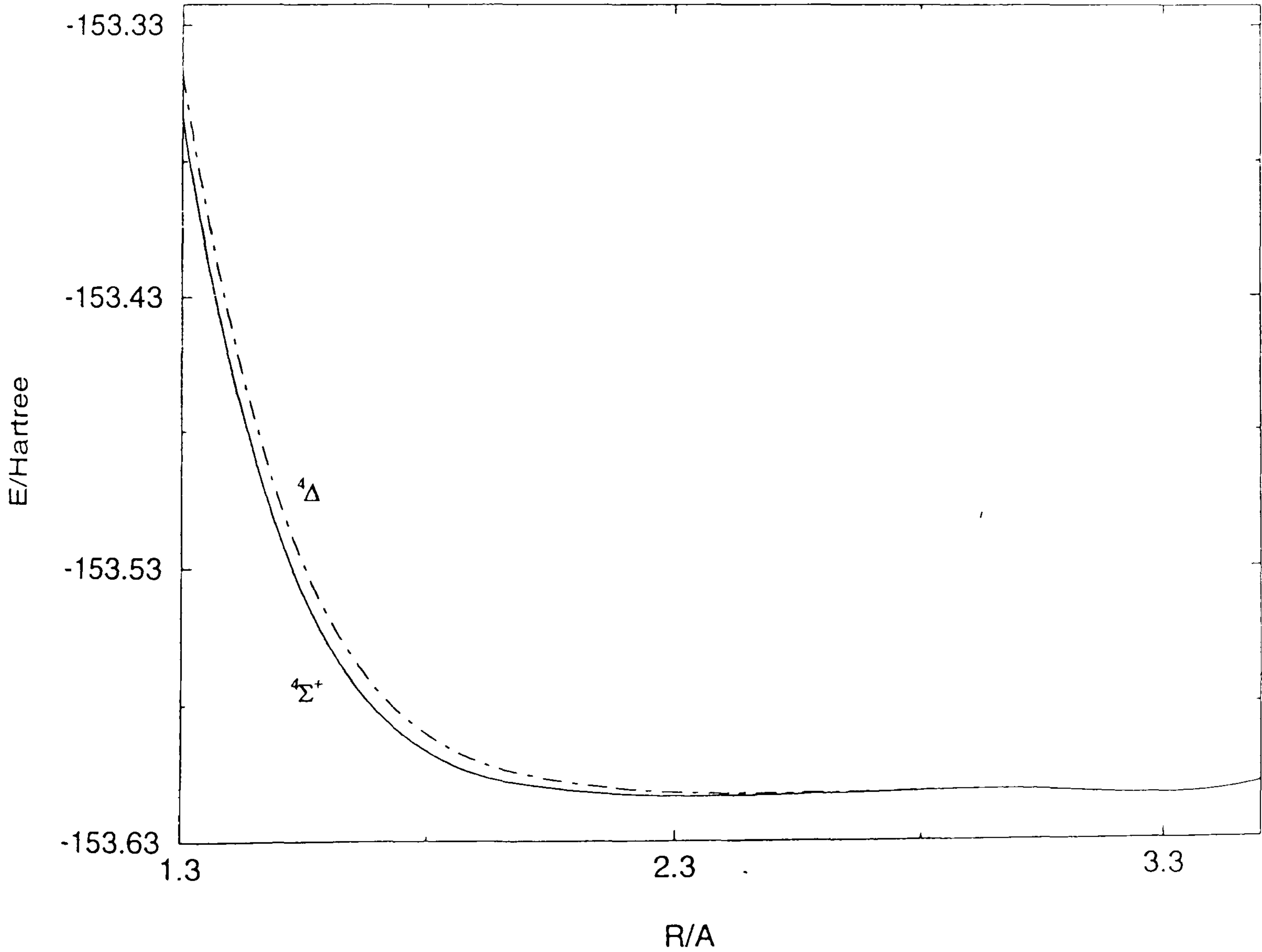
R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.3	-153.367146	-153.351450	-153.323367	-153.322427	-152.989275
1.4	-153.460042	-153.444900	-153.353749	-153.350656	-153.146610
1.5	-153.521993	-153.509635	-153.366623	-153.364098	-153.259505
1.6	-153.561572	-153.551579	-153.374023	-153.372267	-153.339148
1.7	-153.586119	-153.578086	-153.396669	-153.380023	-153.377298
1.8	-153.600915	-153.594515	-153.435481	-153.386200	-153.384079
1.9	-153.609501	-153.604470	-153.462778	-153.392922	-153.390741
2.0	-153.613459	-153.609778	-153.482131	-153.401364	-153.394309
2.25	-153.617653	-153.615962	-153.506662	-153.417860	-153.414741
2.5	-153.617613	-153.616867	-153.514918	-153.423803	-153.421031
2.75	-153.616475	-153.616139	-153.517181	-153.425255	-153.422545
3.0	-153.615781	-153.615617	-153.517823	-153.425691	-153.422921
3.5	-153.613973	-153.613904	-153.516806	-153.424681	-153.421766

$^4\Sigma^+$

$^4\Delta$

E/Hartree

Figure 4.1.5 Calculated potential energy curves



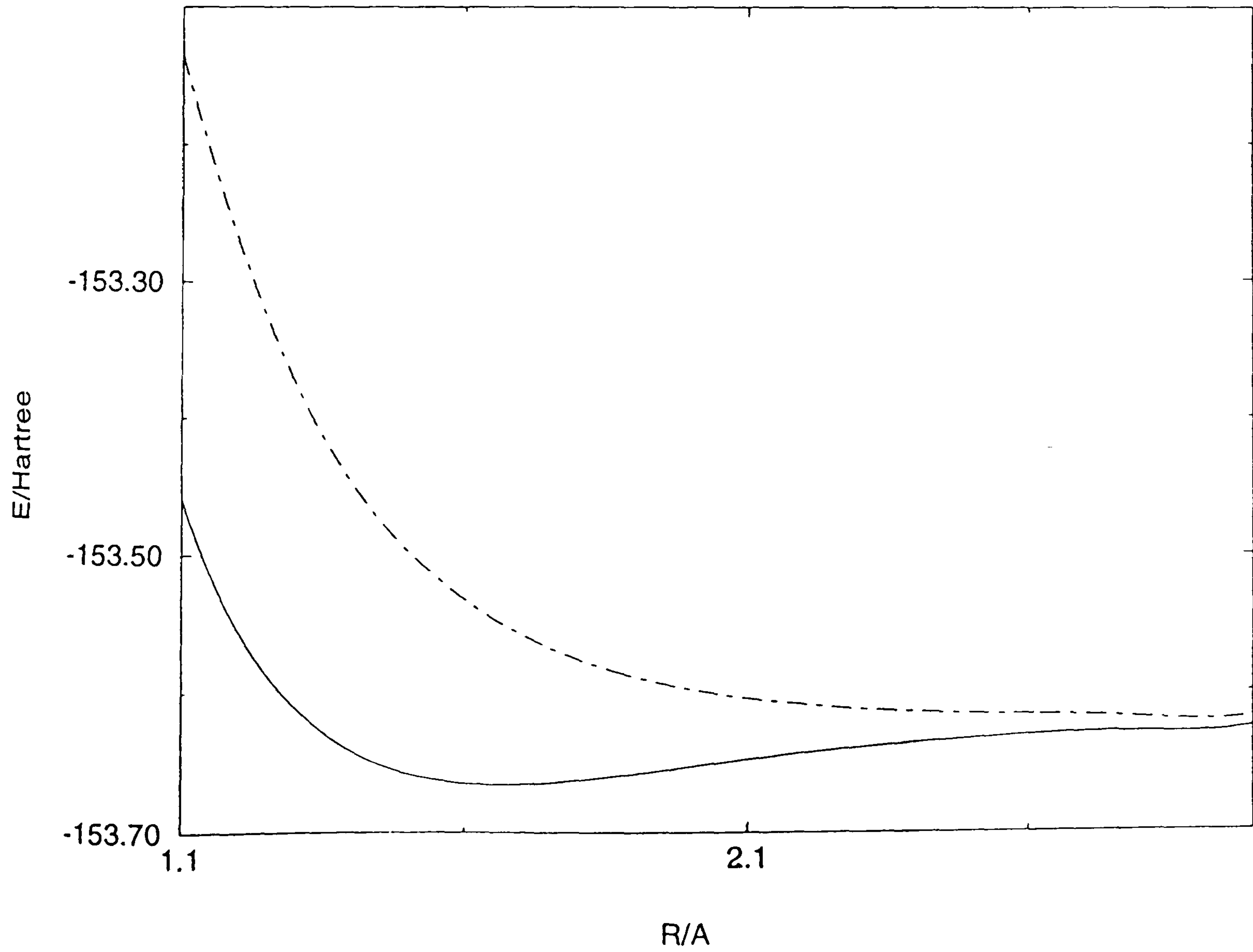
4.1.6 The CI results for the ${}^4\Pi$ states of NF^+ with the VQZ basis sets

4.1.6 Theoretical energy values

R/Å	ROOT1	ROOT2
1.10	-153.462248	-153.138666
1.20	-153.558202	-153.271355
1.30	-153.613166	-153.375558
1.40	-153.644287	-153.448370
1.50	-153.660581	-153.498949
1.60	-153.667275	-153.534646
1.70	-153.667959	-153.560007
1.80	-153.665232	-153.578212
1.90	-153.660790	-153.591294
2.00	-153.655726	-153.600592
2.10	-153.650727	-153.607119
2.20	-153.646167	-153.611657
2.30	-153.642212	-153.614794
2.40	-153.638893	-153.616955
2.50	-153.636168	-153.618447
2.75	-153.631424	-153.620486
3.00	-153.628661	-153.621378

E/Hartree

Figure 4.1.6 Calculated potential energy curves



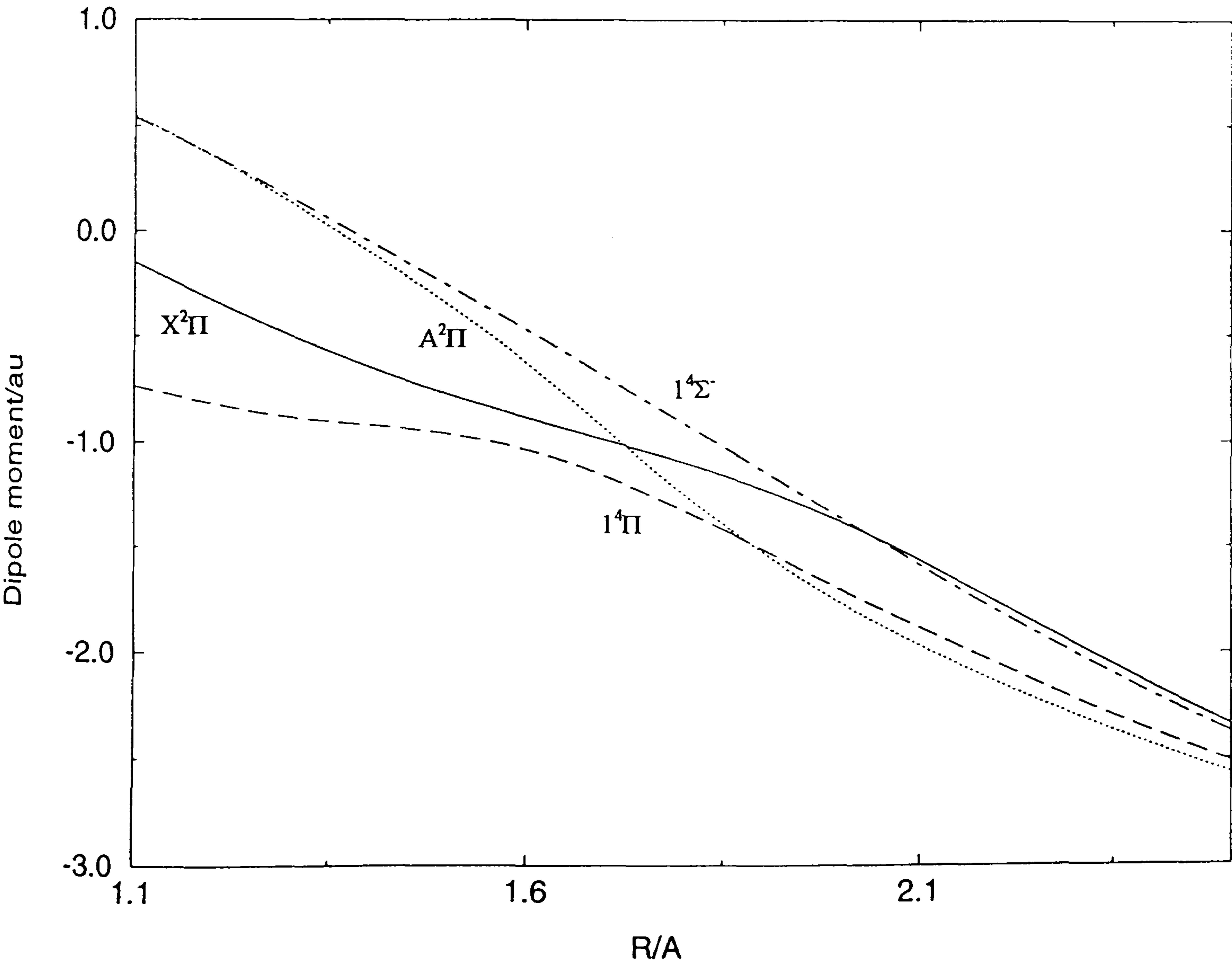
4.1.7 Dipole moments for the bound states of NF^+

Table 4.1.7 Dipole moment values

R/Å	$X^2\Pi$	$A^2\Pi$	$1^4\Pi$	$1^4\Sigma^-$
1.1	-0.147	0.546	-0.734	0.539
1.2	-0.325	0.357	-0.817	0.361
1.3	-0.493	0.140	-0.882	0.162
1.4	-0.642	-0.096	-0.918	-0.046
1.5	-0.771	-0.347	-0.960	-0.257
1.6	-0.885	-0.626	-1.038	-0.472
1.7	-0.992	-0.939	-1.163	-0.691
1.8	-1.101	-1.250	-1.329	-0.913
1.9	-1.228	-1.530	-1.515	-1.139
2.0	-1.383	-1.767	-1.703	-1.364
2.1	-1.563	-1.966	-1.881	-1.586
2.2	-1.759	-2.138	-2.051	-1.800
2.3	-1.958	-2.292	-2.216	-2.003
2.4	-2.153	-2.433	-2.368	-2.194
2.5	-2.338	-2.567	-2.512	-2.373

Dipole moment / au

Figure 4.1.7 Electronic dipole moment functions



4.1.8 Electronic transition moments for NF^+

Table 4.1.8 Transition moment values

$R/\text{\AA}$	$A^2\Pi \rightarrow X^2\Pi$	$1^4\Sigma^- \rightarrow 1^4\Pi$
1.0	-0.022	-0.216
1.1	-0.062	-0.202
1.2	-0.104	-0.185
1.3	-0.147	-0.162
1.4	-0.191	-0.136
1.5	-0.234	-0.110
1.6	-0.270	-0.085
1.7	-0.287	-0.063
1.8	-0.270	-0.046
1.9	-0.226	-0.032
2.0	-0.168	-0.021
2.1	-0.113	-0.010
2.2	-0.070	0.000
2.3	-0.039	0.007
2.4	-0.019	0.006

Electronic transition moment / au

Figure 4.1.8 Electronic transition moments

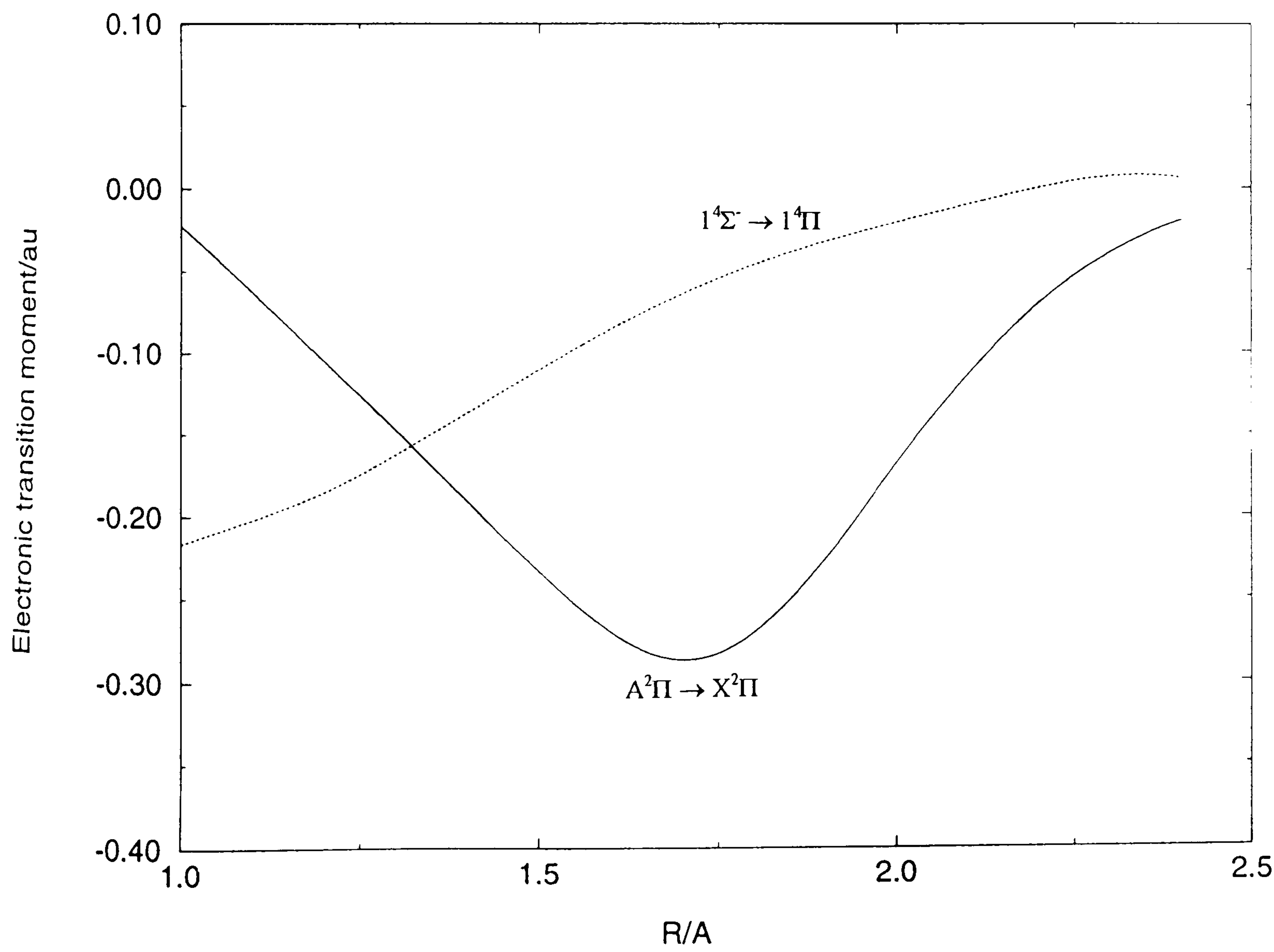
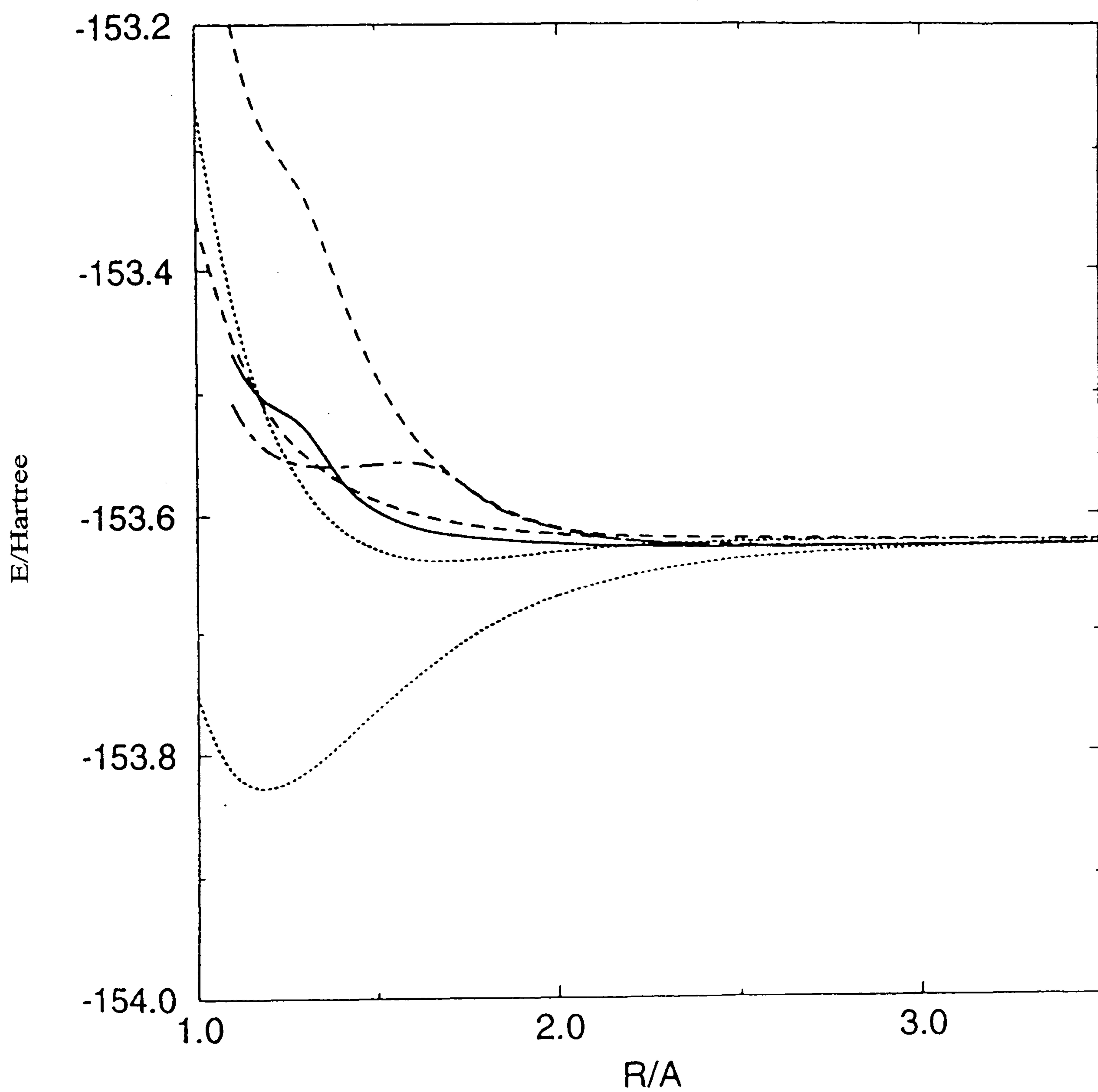
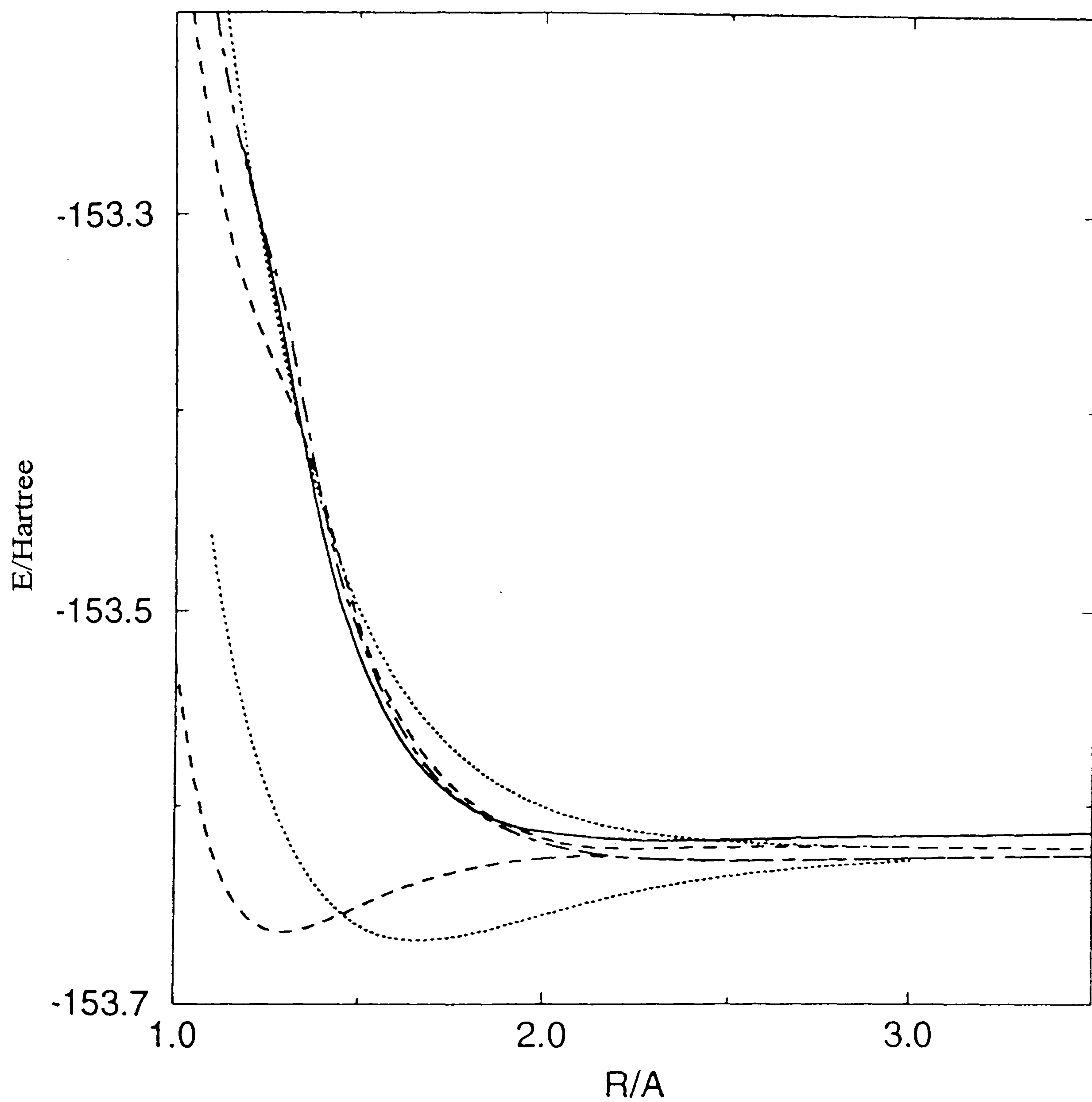


Figure 4.1.9 Calculated potential-energy curves for the doublet states of NF^+



$^2\Sigma^+$ (—), $^2\Pi$ (·····), $^2\Sigma^-$ (----) and $^2\Delta$ (- - - -)

Figure 4.1.10 Calculated potential-energy curves for the quartet states of NF^+



$4\Sigma^+$ (—), 4Π (·····), $4\Sigma^-$ (---) and 4Δ (-.-.-)

Table 4.1.1.7.A Spectroscopic constants for NF⁺

	$r_e/\text{\AA}$	$E/\text{Hartree}^a$	T_e/eV	μ_e/au^b	ω_e/cm^{-1}	$\omega_{x_0}/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_3/cm^{-1}	α_0/cm^{-1}
X ² Π	1.185	-153.827124	0	-0.299	1561.37	13.80	1.481	1.463	1.445	1.490	0.018
	1.180 ^c				1520	10					
	1.182 ^d				1493						
A ² Π	1.695	-153.638655	5.128	-0.923	560.97	16.27	0.718	0.700	0.680	0.728	0.019
		(-153.511112)									
² Δ		-153.543825									
² Σ ⁺		-153.504187									
¹ Σ ⁻		-153.509087									
² Σ ⁻		-153.281023									
¹ Π	1.665	-153.668219	4.324	-0.614	618.54	8.61	0.749	0.737	0.724	0.756	0.013
		(-153.547006)									
¹ Σ ⁻	1.295	-153.663846	4.442	-0.04	1018.39	24.50	1.229	1.198	1.167	1.245	0.031
		(-153.653597)									
² Σ ⁻		-153.333299									
⁴ Δ		-153.270231									
⁴ Σ ⁺		-153.267099									
² Π		-153.252719									

^aEnergies are in $E = \text{hartree} \approx 4.35975 \times 10^{-18} \text{ J}$; energies in parentheses are vertical energies for the bound states mentioned above calculated at $r = 1.185 \text{ \AA}$. ^bWith respect to the centre of mass and with the direction NF; $\text{au} = ea_0 \approx 8.4784 \times 10^{-30} \text{ Cm}$.
^cExperimental data [7]. ^dTheoretical values [57].

4.2.1 The results for PCI^+

As in the case of NF^+ , with the help of the MOLPRO suite of programs [156] all the calculations have been performed using the correlation-consistent valence quadruple-zeta (cc:qvz) basis sets devised by Dunning [157] and Woon and Dunning [158]. The sp basis sets comprised a 16s11p basis contracted to 6s5p with the addition of the same numbers of d, f and g functions as in the NF^+ case. The total number of contracted Gaussian functions is 118. For each spin and symmetry species state averaged CASSCF calculations [146,147] were performed to obtain molecular orbitals for subsequent CI calculations and state averaging was done over all the states of interest in state averaged CASSCF calculations. The active space consisted of the valence orbitals $7\sigma - 10\sigma$, 3π , 4π . Multi-reference CI calculations have been made with the internally contracted CI method of Knowles and Werner [150,151] in which the sets of reference configurations were those used in the CASSCF calculations. Table 4.2 gives details of the numbers of roots considered (A), the sizes of the reference spaces (B), the numbers of contracted (C) and uncontracted (D) configurations.

Table 4.2 Details of configuration interaction calculations

State	A	B	C	D
$^2\Sigma^+$	2	264	232564	7613384
$^2\Pi$	2	252	232860	7016380
$^2\Sigma^-$	5	240	480352	6410288
$^4\Sigma^+$	2	108	213268	6082652
$^4\Pi$	2	126	213854	5983882
$^4\Sigma^-$	3	144	296980	5682628

The results obtained in the CI calculations with the VQZ basis sets are given in tables and figures 4.2.1 to 4.2.6 for the $^2\Pi$, $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^-$, $^4\Sigma^+$ and $^4\Pi$ states, respectively. The dominant configurations for each of the six states are, in turn, given in tables 4.1.2.1.A to 4.1.2.6.A. These show how the configurations change at avoided crossings. In the region of the equilibrium bond length ($r = 1.915 \text{ \AA}$) for the $X^2\Pi$ state the 7σ and 8σ orbitals are predominantly Cl $3s$ and P $3s$ respectively. The orbitals 9σ and 10σ are bonding and antibonding combinations of predominantly $3p_\sigma$ orbitals. On the other hand, the orbitals 3π and 4π are bonding and antibonding combinations of the $3p_\pi$ orbitals. The chlorine atom orbitals have the larger weight in the 3π orbital and phosphorus in the 4π orbital. As the internuclear distance becomes longer the orbitals 9σ and 3π correlate with $3p_\sigma$ and $3p_\pi$ orbitals on Cl and the orbitals 10σ , 4π with $3p_\sigma$ and $3p_\pi$ orbitals on P.

As in the case of NF^+ , these calculations were carried out under C_{2v} symmetry and the Σ^+ (or Σ^-) calculation generates both Σ^+ (or Σ^-) and Δ wavefunctions.

As shown in figure 2, a Δ state arises from the combination of $\text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P})$. Thus, as mentioned in the previous subsections 4.1.1.2 to 4.1.1.5 for $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^-$ and $^4\Sigma^+$ states respectively, we have examined the wavefunctions and characterised the states accordingly.

The wavefunctions have been examined and labelled as Σ or Δ not only for PCl^+ but also for AsCl^+ and BBr^+ as will be discussed in the following sections 4.1.3 and 4.1.4.

The preliminary calculations using the VDZ and VTZ basis sets have not been examined as mentioned in subsection 4.1.1.2.

4.1.2.1 The CI calculations for the $^2\Pi$ states of PCI^+ with the VQZ basis sets

The energy values obtained and the corresponding potential-energy curves are given in table 4.2.1 and figure 4.2.1. The dominant configurations for the $^2\Pi$ states are given in table 4.1.2.1.A

Table 4.1.2.1.A Dominant configurations for the $^2\Pi$ state

State	Configuration	Bond length
$1^2\Pi$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 3\pi^4 4\pi^1$	
$2^2\Pi$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 3\pi^3 4\pi^2$	

From figure 4.2.1 the two potential curves generated represent bound states. Root1($1^2\Pi$) has quite a deep well and Root2($2^2\Pi$) is bound. Thus, spectroscopic constants have been calculated for both states and also experimental data [8,9] for the two states have been obtained. The calculated and experimental values are presented in table 4.1.2.1.B and the comparison of our values with experimental data [8,9] are given as follows.

Table 4.1.2.1.B Spectroscopic constants for the $^2\Pi$ state

CONSTS	EXPT. ($1^2\Pi$)	ROOT1($1^2\Pi$)	EXPT. ($2^2\Pi$)	ROOT2($2^2\Pi$)
ω_e/cm^{-1}	689.8^d	681.32	320.6^d	312.81
$\omega_e x_e/\text{cm}^{-1}$	2.60^d	2.63		1.51
B_0/cm^{-1}		0.279	0.188^c	0.183
B_1/cm^{-1}		0.277	0.187^c	0.181
B_2/cm^{-1}		0.276		0.180
B_e/cm^{-1}	0.284^c	0.280		0.183
α_e/cm^{-1}	${}^c1.47 \times 10^{-3}$	1.52×10^{-3}		0.001
$R_e/\text{\AA}$	1.900^c	1.915	2.334^c	2.365

^cExperimental data from reference [9]. ^dExperimental values from reference [8].

For the $1^2\Pi$ state, the calculated vibrational constant (ω_e), anharmonicity constant ($\omega_e x_e$), rotational constant (B_e), vibrational-rotational constant (α_e) and bond length (R_e) differ from experimental values [8,9] by 1.23 %, 1.15 %, 1.41 %, 3.40 % and 0.79 %. There is good agreement between theory and experiment for root1.

In the case of the $2^2\Pi$ state, the computed vibrational constant (ω_e), rotational constant (B_0), rotational constant (B_1) and bond length (R_e) are in reasonable agreement with the experimental parameters with the errors of 2.43 %, 2.66 %, 3.21 % and 1.33 %.

4.1.2.2 The CI calculations for the $^2\Sigma^+$ states of PCl^+ with the VQZ basis sets

The energy values calculated and the potential-energy curves for the 2 states considered given are in table 4.2.2 and figure 4.2.2.

As earlier stated, the wavefunctions have been examined and assigned as Σ^+ or Δ .

Thus, roots 1 and 2 correspond to a $^2\Sigma^+$ state and a $^2\Delta$ state respectively. As the bond length changes the dominant configurations obtained are given in table 4.1.2.2.A.

Table 4.1.2.2.A Dominant configurations for the $^2\Sigma^+$ state

State	Configuration	Bond length
$^2\Sigma^+$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^1 3\pi^4 4\pi^2$	$r \leq 1.6 \text{ \AA}$
	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^1 3\pi^4$	$1.7 \leq r \leq 2.75 \text{ \AA}$
	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^1 3\pi^3 4\pi^1$	$r \geq 3.0 \text{ \AA}$
$^2\Delta$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^1 3\pi^4 4\pi^2$	$r \leq 2.4 \text{ \AA}$
	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^1 3\pi^3 4\pi^1$	$r \geq 2.5 \text{ \AA}$

As shown in figure 4.2.2, there are no bound states for this symmetry. Root1 has a very shallow minimum and root2 is repulsive. Therefore, no spectroscopic constants have been calculated. Furthermore, no experimental spectroscopic data are available.

4.1.2.3 The CI calculations for the $^2\Sigma^-$ states of PCl^+ with the VQZ basis sets

Here, the same problem as for the $^2\Sigma^-$ state for NF^+ occurred. Thus, to eliminate convergence problems 5 states have been calculated rather than 3 states arising from the combination of $\text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P})$ as presented in figure 1. Table 4.2.3 gives the energies of the five roots at each bond length and the first three roots considered have been chosen, examined and labelled. Figure 4.2.3 shows the three corresponding potential energy curves. Root1 and root3 are $^2\Sigma^-$ states and root2 is a $^2\Delta$ state. Table 4.1.2.3.A gives the dominant configurations for the $^2\Sigma^-$ states as the bond length is varied.

Table 4.1.2.3.A Dominant configurations for the $^2\Sigma^-$ state

State	Configuration	Bond length
$1^2\Sigma^-$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^1 3\pi^4 4\pi^2$	
$2^2\Sigma^-$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^1 3\pi^3 4\pi^3$	$r \leq 1.8 \text{ \AA}$
	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^1 3\pi^3 4\pi^1$	$r \geq 1.9 \text{ \AA}$

For the $^2\Delta$ state the dominant configurations are as given in Table 4.1.2.2.A. From figure 4.2.3 it can be seen that the three roots are repulsive and for these three states no spectroscopic constants have been calculated and there are no experimental data.

4.1.2.4 The CI calculations for the $^4\Sigma^-$ states of PCI^+ with the VQZ basis sets

The energies obtained for the three roots and the corresponding three potential energy curves, labelled $^4\Sigma^-$ and $^4\Delta$ accordingly, are given in table 4.2.4 and figure 4.2.4.

Roots 1 and 3 are $^4\Sigma^-$ states and root2 is a $^4\Delta$ state. For these three states the dominant configurations are given in table 4.1.2.4.A.

Table 4.1.2.4.A Dominant configurations for the $^4\Sigma^-$ states

State	Configuration	Bond length
$1^4\Sigma^-$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^1 3\pi^4 4\pi^2$	
$2^4\Sigma^-$	$\cdots 7\sigma^2 8\sigma^1 9\sigma^2 3\pi^4 4\pi^2$	$r \leq 1.9 \text{ \AA}$
	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^1 3\pi^3 4\pi^1$	$r \geq 2.0 \text{ \AA}$
$^4\Delta$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^1 3\pi^3 4\pi^3$	$r \leq 1.6 \text{ \AA}$
	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^1 3\pi^3 4\pi^1$	$r \geq 1.8 \text{ \AA}$

As shown in figure 4.2.4, root1 is reasonably bound whereas roots 2 and 3 are repulsive. Thus, spectroscopic constants have been computed only for the $1^4\Sigma^-$ state and are reported in table 4.1.2.4.B.

Table 4.1.2.4.B Spectroscopic constants of the $1^4\Sigma^-$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$1^4\Sigma^-$	427.56	5.98	0.245	0.242	0.238	0.246	0.003	2.04

In contrast, there are no experimental spectroscopic data for the $1^4\Sigma^-$ state.

Therefore, the calculated constants for the $1^4\Sigma^-$ state can be regarded as predictions for the experimental constants.

4.1.2.5 The CI calculations for the $^4\Sigma^+$ states of PCI^+ with the VQZ basis sets

The energy values obtained, the corresponding potential energy curves and the dominant configurations for this state are given in table 4.2.5, figure 4.2.5 and

4.1.2.5.A respectively.

Table 4.1.2.5.A Dominant configurations for the $^4\Sigma^+$ state

State	Configuration	Bond length
$^4\Sigma^+$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^1 3\pi^3 4\pi^1$	$r \leq 1.4 \text{ \AA}, r \geq 1.7 \text{ \AA}$
	$\cdots 7\sigma^2 8\sigma^2 9\sigma^1 3\pi^3 4\pi^3$	$1.5 \text{ \AA} \leq r \leq 1.6 \text{ \AA}$

For the $^4\Delta$ state the dominant configurations are as for the $^4\Sigma^-$ state given in the previous section. Neither the $^4\Sigma^+$ nor the $^4\Delta$ states are bound. Thus, no spectroscopic constants have been determined. Also, there are no experimental data for these states.

4.1.2.6 The CI calculations for the $^4\Pi$ states of PCI^+ with the VQZ basis sets

The energies, the two potential energy curves and the dominant configurations are reported in table 4.2.6, figure 4.2.6 and table 4.1.2.6.A respectively.

Table 4.1.2.6.A Dominant configurations for the $^4\Pi$ state

State	Configuration	Bond length
$1^4\Pi$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^2 3\pi^3 4\pi^2$	$r \geq 1.4 \text{ \AA}$
$2^4\Pi$	$\cdots 7\sigma^2 8\sigma^2 9\sigma^1 10\sigma^1 3\pi^4 4\pi^1$	$r \geq 1.4 \text{ \AA}$

The $1^4\Pi$ state is a bound state and the $2^4\Pi$ state is repulsive. Thus, spectroscopic constants for $1^4\Pi$ state have been calculated and are reported in table 4.1.2.6.B.

Table 4.1.2.6.B Spectroscopic constants of the $1^4\Pi$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$1^4\Pi$	339.10	3.17	0.189	0.187	0.185	0.189	0.002	2.325

Since no spectroscopic parameters have been determined experimentally our calculated values can be used for the prediction of experimental data.

4.1.2.7 General discussion for PCl^+

For the doublet and quartet states the theoretical potential-energy curves are given in figures 4.2.9 and 4.2.10 respectively. As in the case of NF^+ , we have obtained only four bound states, namely $X^2\Pi$, $A^2\Pi$ from the doublet states, $1^4\Sigma^-$ and $1^4\Pi$ from the quartet states. Unlike the $X^2\Pi$ state, other three states are weakly bound. The ground state, $X^2\Pi$, is the lowest root ($1^2\Pi$) which gives an equilibrium bond length of $r = 1.915 \text{ \AA}$. The next dissociation asymptote $\text{Cl}(^2\text{P}) + \text{P}^+(^1\text{D})$ lies higher than $\text{Cl}(^2\text{P}) + \text{P}^+(^3\text{P})$ by 1.10 eV. The shoulders in the potential-energy curves for the $^2\Delta$ and $2^2\Sigma^-$ states in the region of $r = 2.4 \text{ \AA}$ and 1.8 \AA respectively arise from avoided intersections with states correlating with the above dissociation asymptote. However, these avoided crossings are not as pronounced as for the $^2\Delta$ and $2^2\Sigma^-$ states of NF^+ . As in the case of NF^+ , the $1^4\Sigma^-$ and $1^4\Pi$ states have very different bond lengths for the potential minima. Thus, the Franck-Condon factors for this transition will be unfavourable. Table 4.1.2.7.A reports the energies of the bound states at their equilibrium bond lengths, the energies for all states relative to the $X^2\Pi$ state at $r_e = 1.915 \text{ \AA}$, T_e values, dipole moments and spectroscopic constants for the bound states. As described in subsection 4.1.2.1, for the $X^2\Pi$ ground state the calculated spectroscopic constants are in excellent agreement with experimental data [8,9], whereas for the $A^2\Pi$ state the agreement between theory and experiment is a little less good. On the other hand, it is very difficult to calculate accurate spectroscopic constants for weakly bound states. Table 4.2.7 and figure 4.2.7 show the dipole

moments and dipole moment functions for the $X^2\Pi$, $A^2\Pi$, $1^4\Sigma^-$ and $1^4\Pi$ states, and table 4.2.8 and figure 4.2.8 present the electronic transition moments and the electronic transition moment functions for the $A^2\Pi \rightarrow X^2\Pi$ and $1^4\Sigma^- \rightarrow 1^4\Pi$ transitions. As the internuclear distance becomes longer the dipole moment functions in figure 4.2.7 are seen to approach linear functions as in the case of NF^+ . Comparison with figure 4.1.8 shows that the electronic transition moments for the $A^2\Pi \rightarrow X^2\Pi$ transitions are of comparable magnitude for NF^+ and PCl^+ in the vicinity of the respective potential minima. There are many points in common between both ions discussed above and the molecular ion PF^+ [1] for which the lowest dissociation asymptote is $P^+(^3P) + F(^2P)$. For the three ions considered, the ground states, $1^2\Pi$, and the weakly bound $1^4\Sigma^-$ and $1^4\Pi$ states with unfavourable Franck-Condon factors are comparable. On the other hand, the $2^2\Pi$ states for NF^+ and PCl^+ are bound states but for PF^+ this state is repulsive. In the case of NCl^+ , quite different behaviour was found because the lowest dissociation limit $N(^4S) + Cl(^3P)$ lies lower than $N(^3P) + Cl(^2P)$ by 1.57 eV. Due to the closeness of two dissociation asymptotes many more bound states arise for NCl^+ than for NF^+ , PF^+ and PCl^+ . As one moves down the periodic table from the first to the second row the effect of additional inner shell electrons is reflected in the closer spacing of the electronic states as we move to the heavier molecular ions. The T_e values for the A states are 5.1 eV, 4.5 eV and 3.5 eV for NF^+ , PF^+ and PCl^+ respectively. For the $X^2\Pi$ states the depths of the potential wells are reduced as one moves down the periodic table from NF^+ to PCl^+ . For values calculated in our work for NF^+ , PF^+ and PCl^+ are 5.5 eV, 5.0 eV and 4.3 eV respectively.

In conclusion, as shown in table 4.1.2.7.A there are only four bound states for PCl^+ which correlate with the lowest dissociation limit. For the $1^4\Sigma^- \rightarrow 1^4\Pi$ transitions it would be expected that Franck-Condon factors are unfavourable. The theoretical constants are in good agreement with experimental parameters for states which have been observed experimentally. Thus, it is believed that our calculated constants will be reasonable predictions for other states.

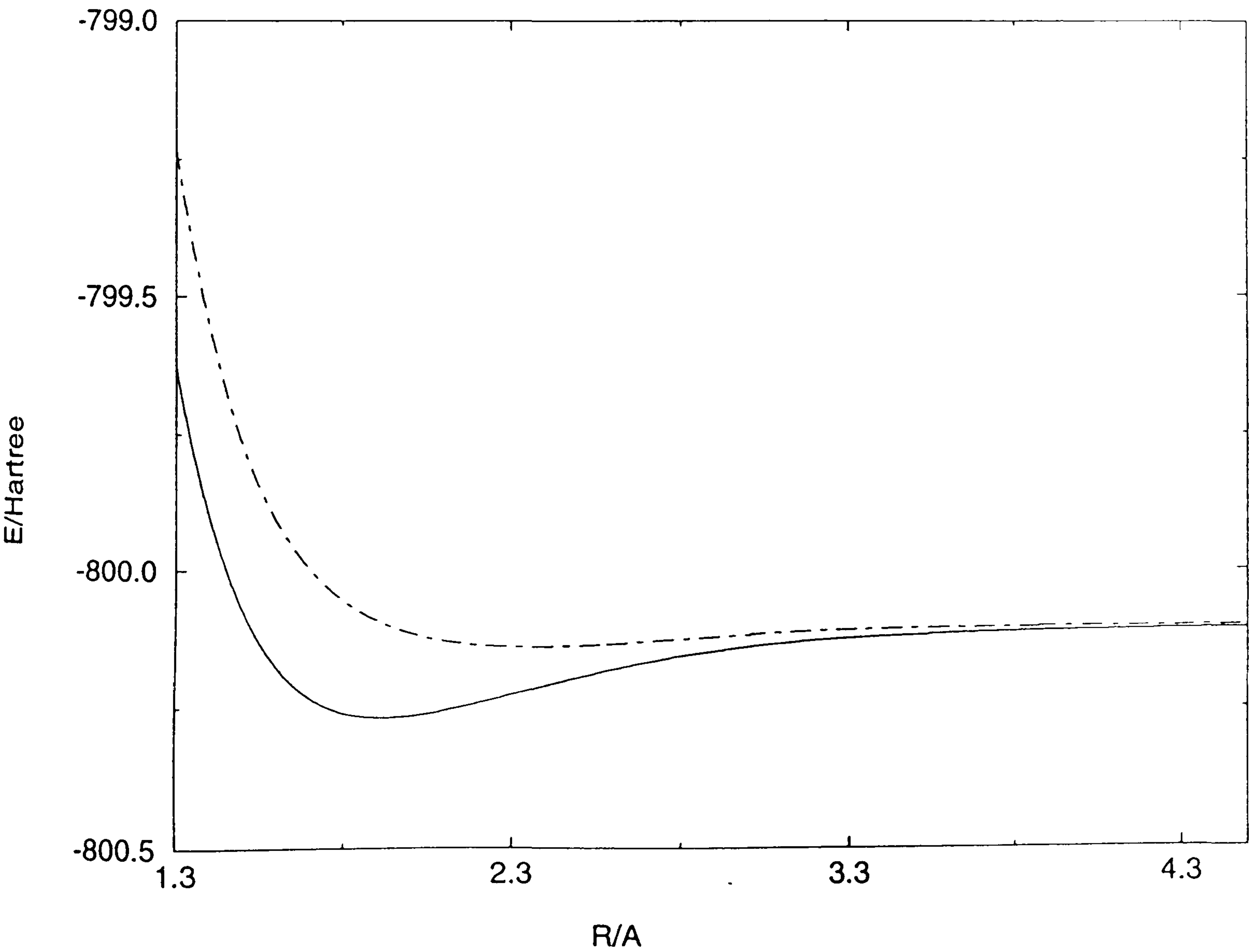
4.2.1 The CI results for the $^2\Pi$ states of PCl^+ with the VQZ basis sets

Table 4.2.1 Theoretical energy values

R/A	ROOT1	ROOT2
1.3	-799.626219	-799.230919
1.5	-800.075156	-799.767797
1.6	-800.175518	-799.905977
1.7	-800.230853	-799.995547
1.8	-800.257478	-800.053412
1.9	-800.265779	-800.090362
2.0	-800.262730	-800.113339
2.1	-800.252915	-800.127010
2.2	-800.239366	-800.134448
2.3	-800.224104	-800.137686
2.4	-800.208485	-800.138079
2.5	-800.193422	-800.136554
2.75	-800.161629	-800.128283
3.0	-800.140318	-800.118644
3.5	-800.119428	-800.107336
4.0	-800.111252	-800.104119
4.5	-800.107464	-800.102989

E/Hartree

Figure 4.2.1 Calculated potential energy curves



4.2.2 The CI results for the $^2\Sigma^+$ states of PCl^+ with the VQZ basis sets

Table 4.2.2 Theoretical energy values

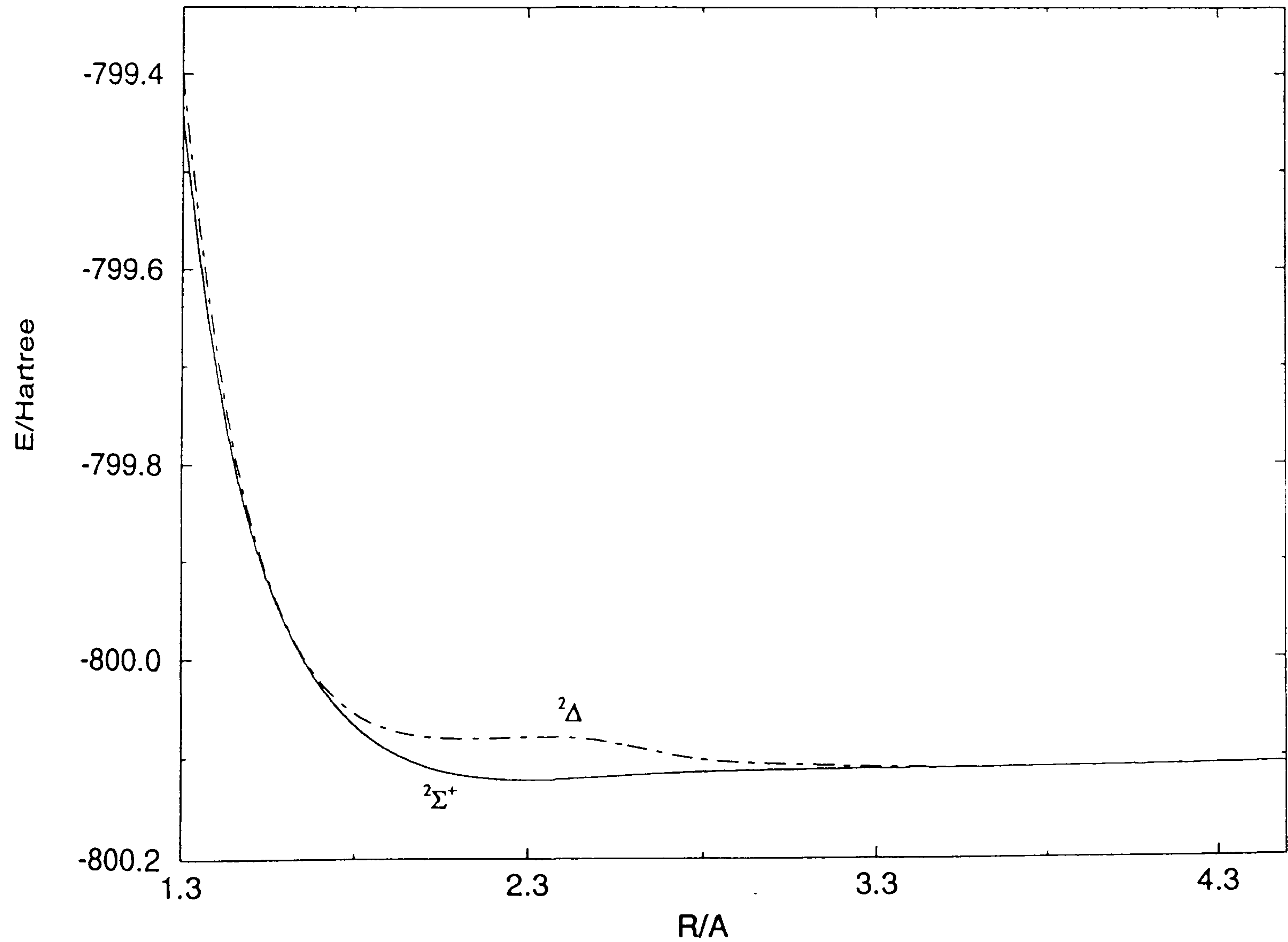
R/Å	ROOT1	ROOT2
1.3	-799.440469	-799.399487
1.5	-799.863729	-799.854600
1.6	-799.962597	-799.959660
1.7	-800.024981	-800.020253
1.9	-800.090877	-800.069769
2.0	-800.107094	-800.077018
2.1	-800.116294	-800.079389
2.2	-800.120618	-800.079391
2.3	-800.121707	-800.078314
2.5	-800.119368	-800.081993
2.75	-800.114718	-800.099217
3.0	-800.112559	-800.106442
3.5	-800.110646	-800.109499
4.0	-800.108770	-800.108460
4.5	-800.106814	-800.106690

$^2\Sigma^+$

$^2\Delta$

E/Hartree

Figure 4.2.2 Calculated potential energy curves



4.2.3 The CI results for the $^2\Sigma^-$ states of PCI^+ with the VQZ basis sets

Table 4.2.3 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.55	-799.875541	-799.913923	-799.692808	-799.689059	-799.631649
1.60	-799.924077	-799.959511	-799.746900	-799.745890	-799.689930
1.70	-799.991847	-800.020163	-799.830032	-799.823008	-799.777045
1.80	-800.033813	-800.053772	-799.882935	-799.876562	-799.852127
1.90	-800.060278	-800.069834	-799.925792	-799.925310	-799.903861
2.00	-800.077120	-800.077271	-799.970766	-799.969423	-799.949126
2.10	-800.087963	-800.079740	-800.005448	-800.006675	-799.983503
2.20	-800.094952	-800.079759	-800.033108	-800.034290	-800.009316
2.30	-800.099422	-800.078690	-800.054014	-800.055178	-800.028386
2.40	-800.102228	-800.077306	-800.070659	-800.069641	-800.042184
2.50	-800.103935	-800.082649	-800.081195	-800.075208	-800.051906
2.75	-800.105655	-800.099406	-800.097991	-800.071738	-800.064199
3.00	-800.106893	-800.106499	-800.103488	-800.070934	-800.069212
3.50	-800.109217	-800.109409	-800.103250	-800.069800	-800.069319
4.00	-800.108287	-800.108412	-800.102906	-800.067698	-800.067489
4.50	-800.107138	-800.107209	-800.102977	-800.066236	-800.066129

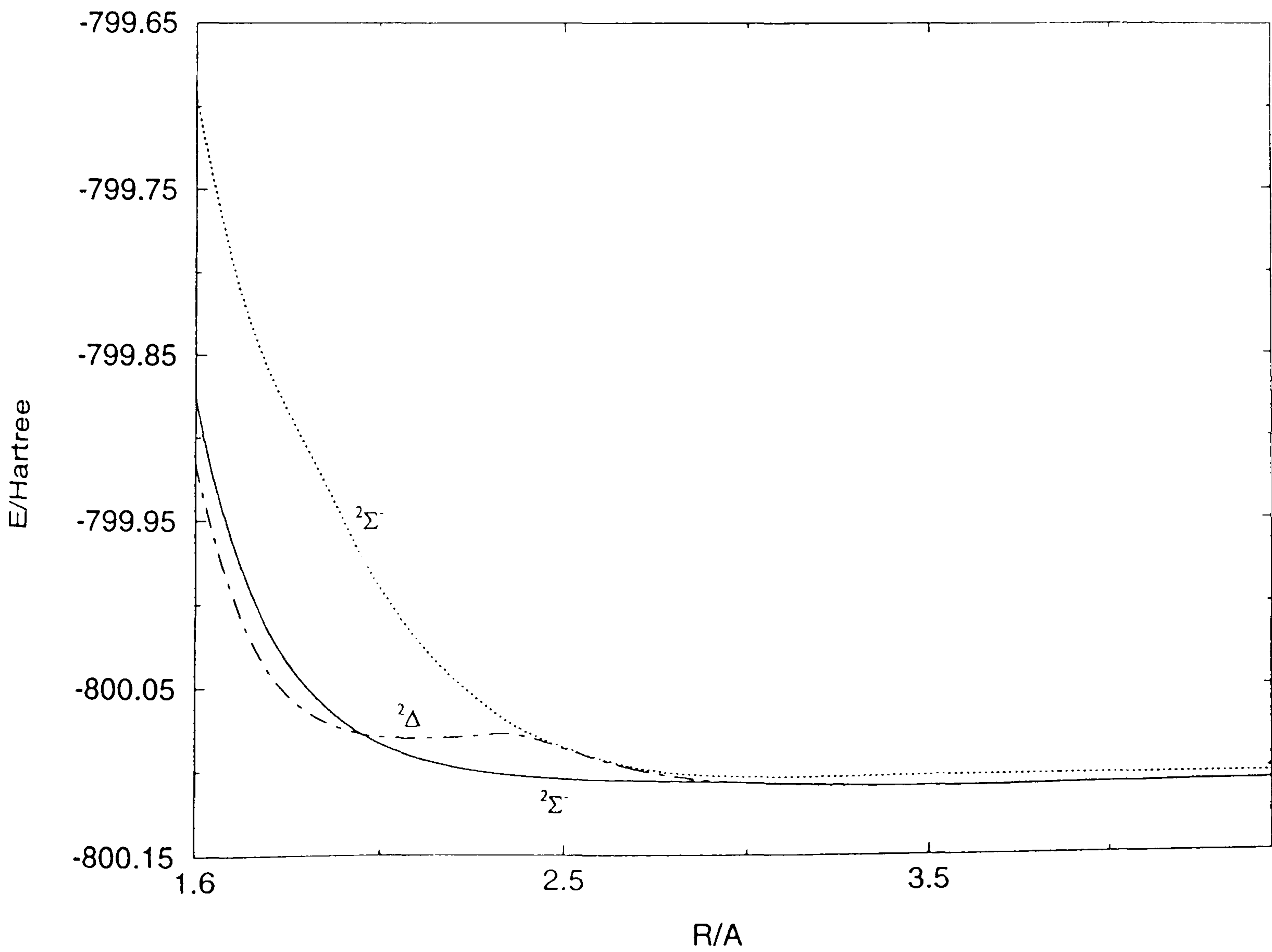
$^2\Sigma^-$

$^2\Delta$

$^2\Sigma^-$

E/Hartree

Figure 4.2.3 Calculated potential energy curves



4.2.4 The CI results for the $^4\Sigma^-$ states of PCl^+ with the VQZ basis sets

Table 4.2.4 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.3	-799.464861	-799.207926	-799.042218
1.5	-799.921811	-799.675320	-799.586427
1.6	-800.027028	-799.791875	-799.725693
1.8	-800.117717	-799.915900	-799.885918
1.9	-800.132962	-799.949880	-799.944128
2.0	-800.138150	-799.989742	-799.985835
2.1	-800.137783	-800.024080	-800.019073
2.2	-800.134790	-800.049725	-800.044959
2.3	-800.130909	-800.068660	-800.064388
2.4	-800.126976	-800.082428	-800.078669
2.5	-800.123341	-800.092261	-800.088961
2.75	-800.116138	-800.105566	-800.103000
3.0	-800.112010	-800.110113	-800.107186
3.5	-800.110476	-800.110310	-800.104697
4.0	-800.108642	-800.108517	-800.103383
4.5	-800.107130	-800.107057	-800.103151

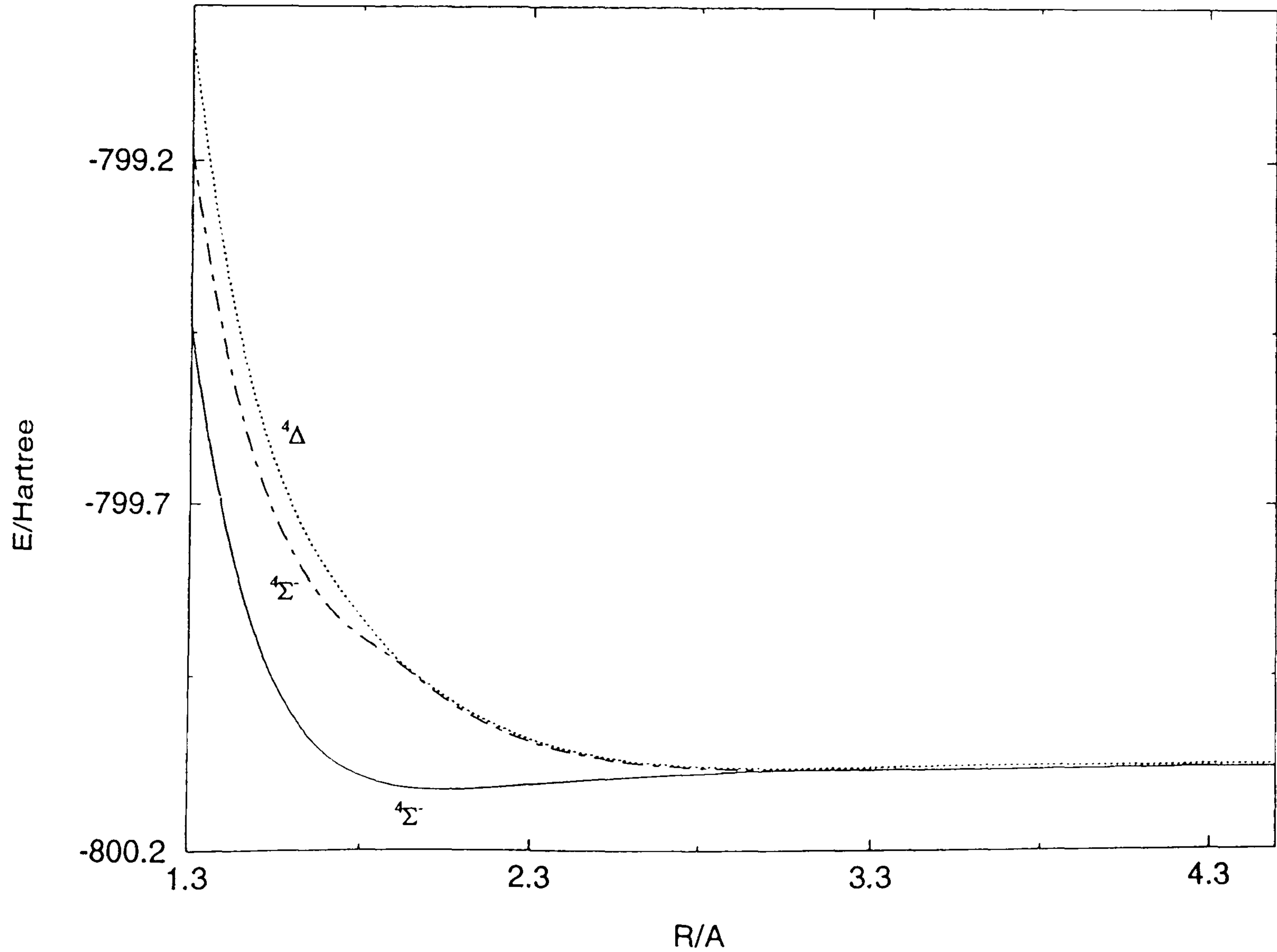
$^4\Sigma^-$

$^4\Sigma^-$

$^4\Delta$

E/Hartree

Figure 4.2.4 Calculated potential energy curves



4.2.5 The CI results for the $^4\Sigma^+$ states of PCl^+ with the VQZ basis sets

Table 4.2.5 Theoretical energy values

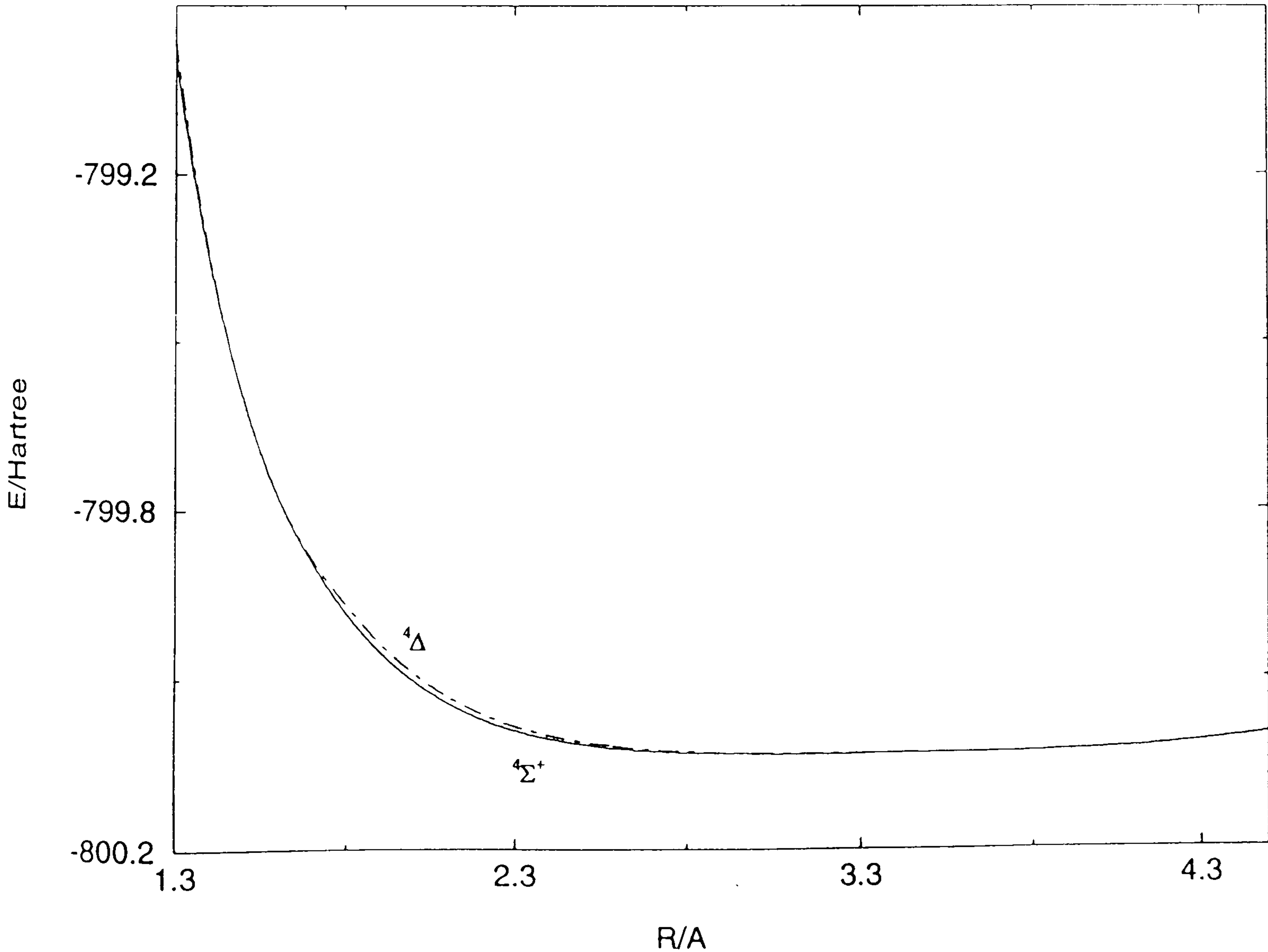
R/Å	ROOT1	ROOT2
1.3	-799.075503	-799.052929
1.5	-799.587803	-799.586886
1.6	-799.728495	-799.727471
1.7	-799.825332	-799.819908
1.8	-799.900871	-799.888066
1.9	-799.958588	-799.945502
2.0	-800.001861	-799.990328
2.1	-800.034137	-800.024364
2.2	-800.057992	-800.049865
2.3	-800.075388	-800.068714
2.4	-800.087862	-800.082433
2.5	-800.096628	-800.092245
2.75	-800.108084	-800.105574
3.0	-800.111581	-800.110155
3.5	-800.110511	-800.110013
4.0	-800.104931	-800.104719
4.5	-800.082193	-800.082084

$^4\Sigma^+$

$^4\Delta$

E/Hartree

Figure 4.2.5 Calculated potential energy curves



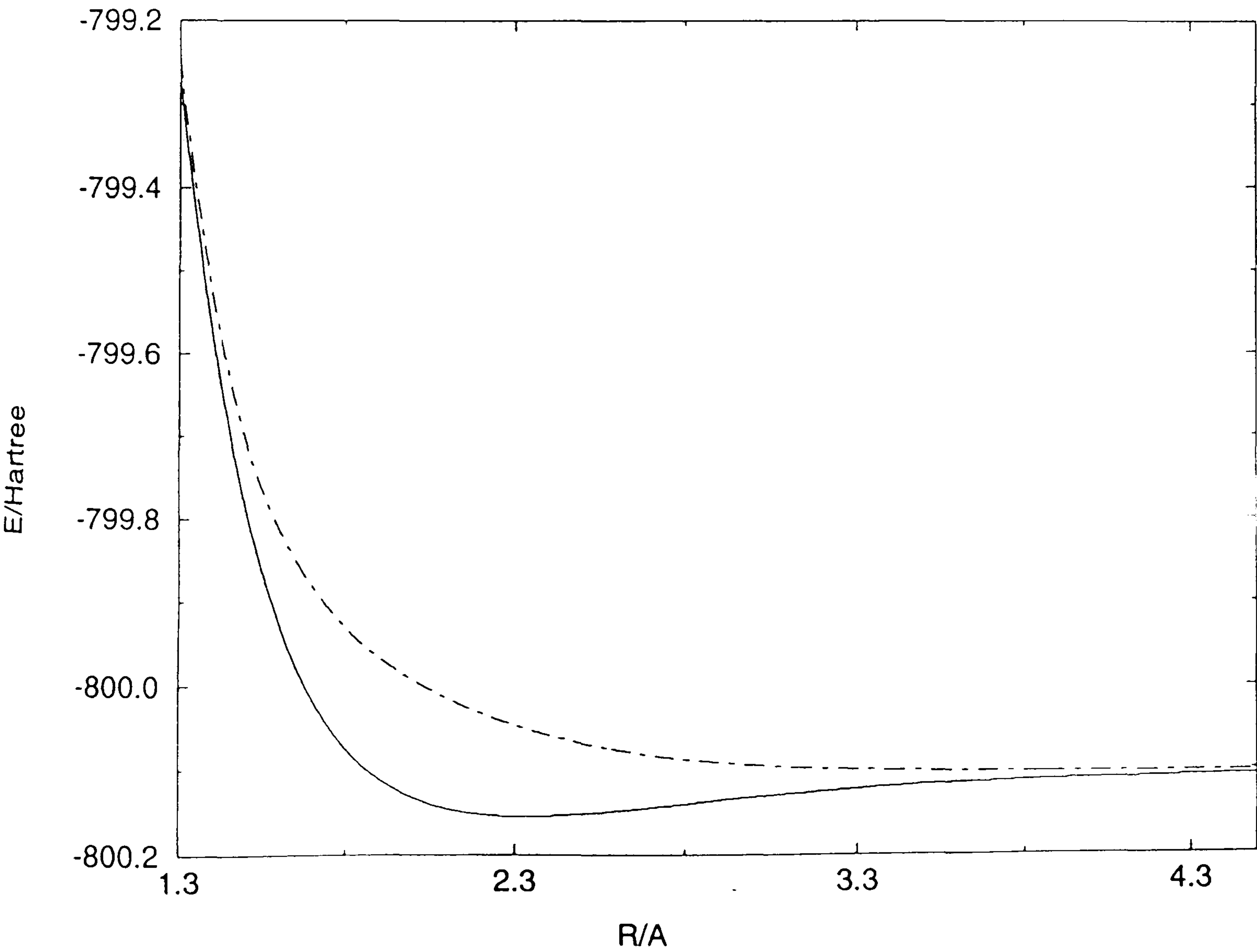
4.2.6 The CI results for the $^4\Pi$ states of PCI^+ with the VQZ basis sets

Table 4.2.6 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-799.264104	-799.243767
1.5	-799.785639	-799.702685
1.6	-799.925103	-799.809772
1.7	-800.015652	-799.880373
1.8	-800.073880	-799.929263
1.9	-800.110682	-799.964825
2.0	-800.133223	-799.991947
2.1	-800.146227	-800.013518
2.2	-800.152836	-800.031190
2.3	-800.155165	-800.045844
2.4	-800.154673	-800.057960
2.5	-800.152383	-800.067881
2.75	-800.142989	-800.085020
3.0	-800.132797	-800.094401
3.5	-800.118055	-800.101401
4.0	-800.110818	-800.102737
4.5	-800.106592	-800.101949

E/Hartree

Figure 4.2.6 Calculated potential energy curves



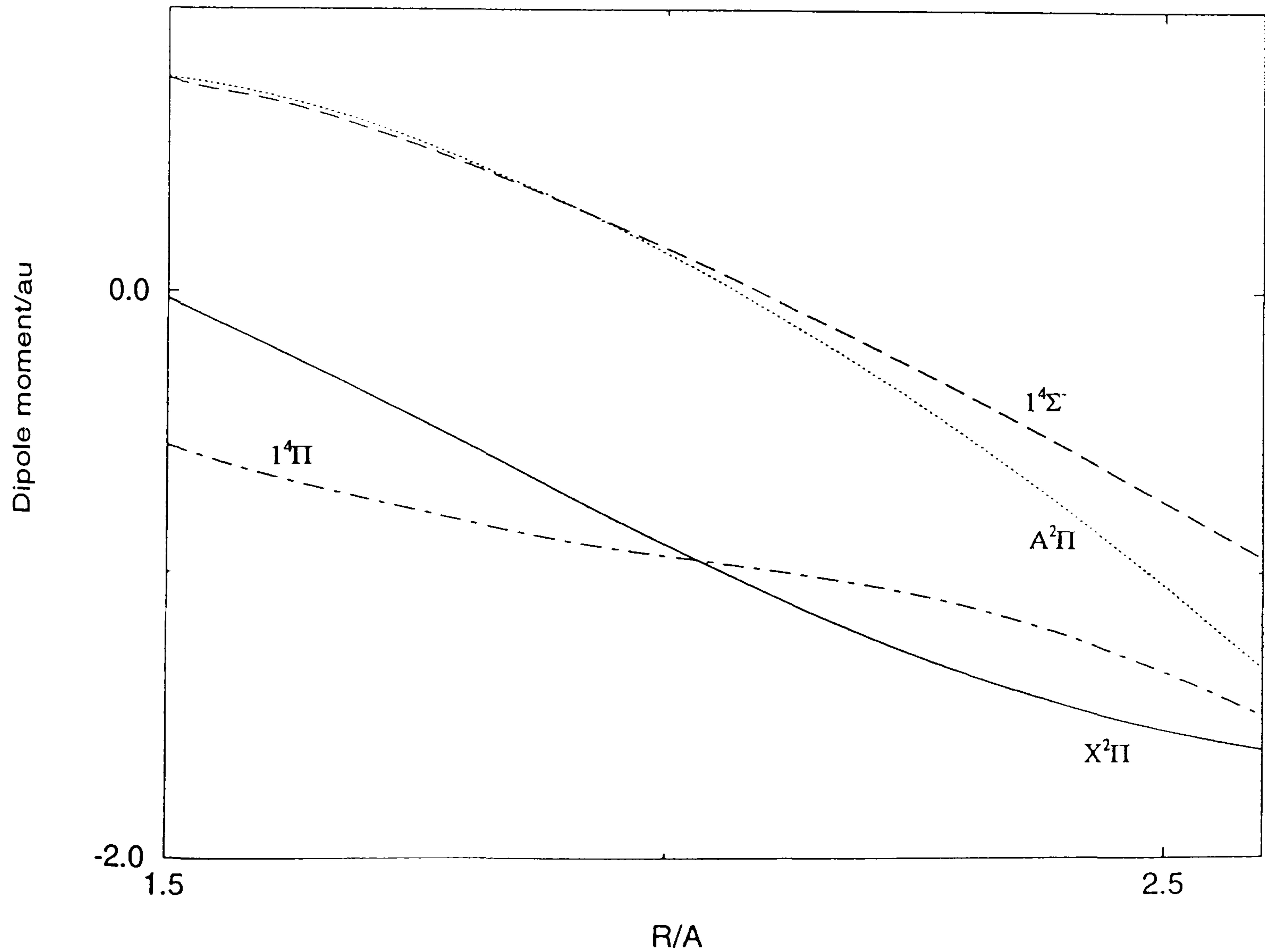
4.2.7 Dipole moments for the bound states of PCl^+

Table 4.2.7 Dipole moment values

R/Å	X ² Π	A ² Π	1 ⁴ Σ ⁻	1 ⁴ Π
1.5	-0.024	0.757	0.753	-0.547
1.6	-0.187	0.698	0.681	-0.650
1.7	-0.359	0.600	0.580	-0.734
1.8	-0.535	0.467	0.455	-0.813
1.9	-0.721	0.312	0.311	-0.886
2.0	-0.902	0.136	0.154	-0.941
2.1	-1.071	0.062	-0.013	-0.989
2.2	-1.224	-0.280	-0.187	-1.044
2.3	-1.356	-0.516	-0.367	-1.118
2.4	-1.468	-0.772	-0.554	-1.219
2.5	-1.557	-1.046	-0.748	-1.350
2.75	-1.713	-1.775	-1.262	-1.768

Dipole moment / au

Figure 4.2.7 Electronic dipole moment functions



4.2.8 Electronic transition moments for PCl^+

Table 4.2.8 Transition moment values

R/Å	$A^2\Pi \rightarrow X^2\Pi$	$1^4\Sigma^- \rightarrow 1^4\Pi$
1.5	-0.017	-0.221
1.6	-0.041	-0.218
1.7	-0.085	-0.211
1.8	-0.126	-0.199
1.9	-0.174	-0.183
2.0	-0.230	-0.164
2.1	-0.290	-0.144
2.2	-0.353	-0.123
2.3	-0.413	-0.102
2.4	-0.467	-0.083
2.5	-0.502	-0.066
2.7	-0.511	-0.037
2.9	-0.405	-0.015
3.1	-0.242	0.004
3.3	-0.117	0.010
3.5	-0.051	0.011

Electronic transition moment / au

Figure 4.2.8 Electronic transition moments

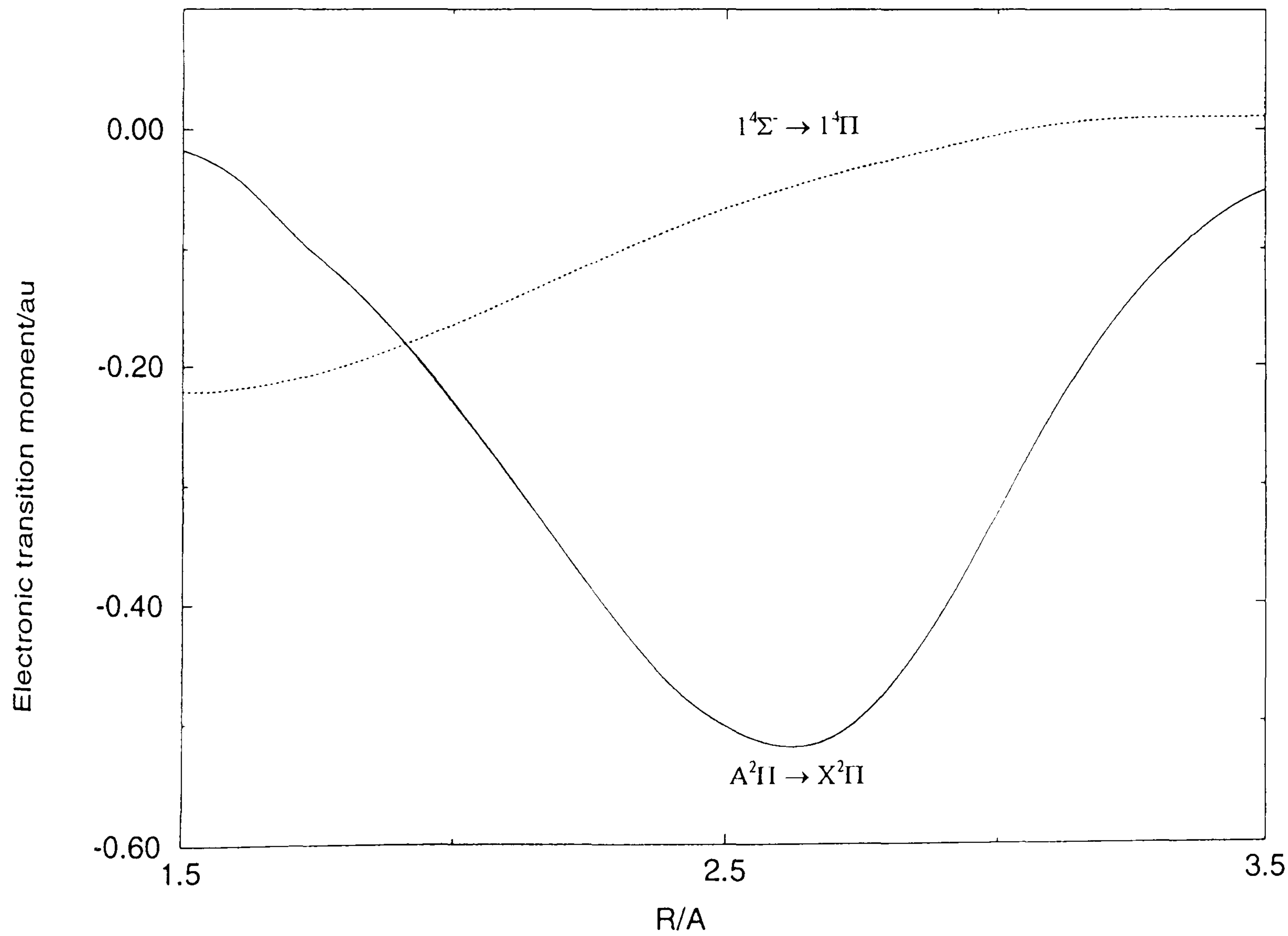


Figure 4.2.9 Calculated potential-energy curves for the doublet states of PCl^+

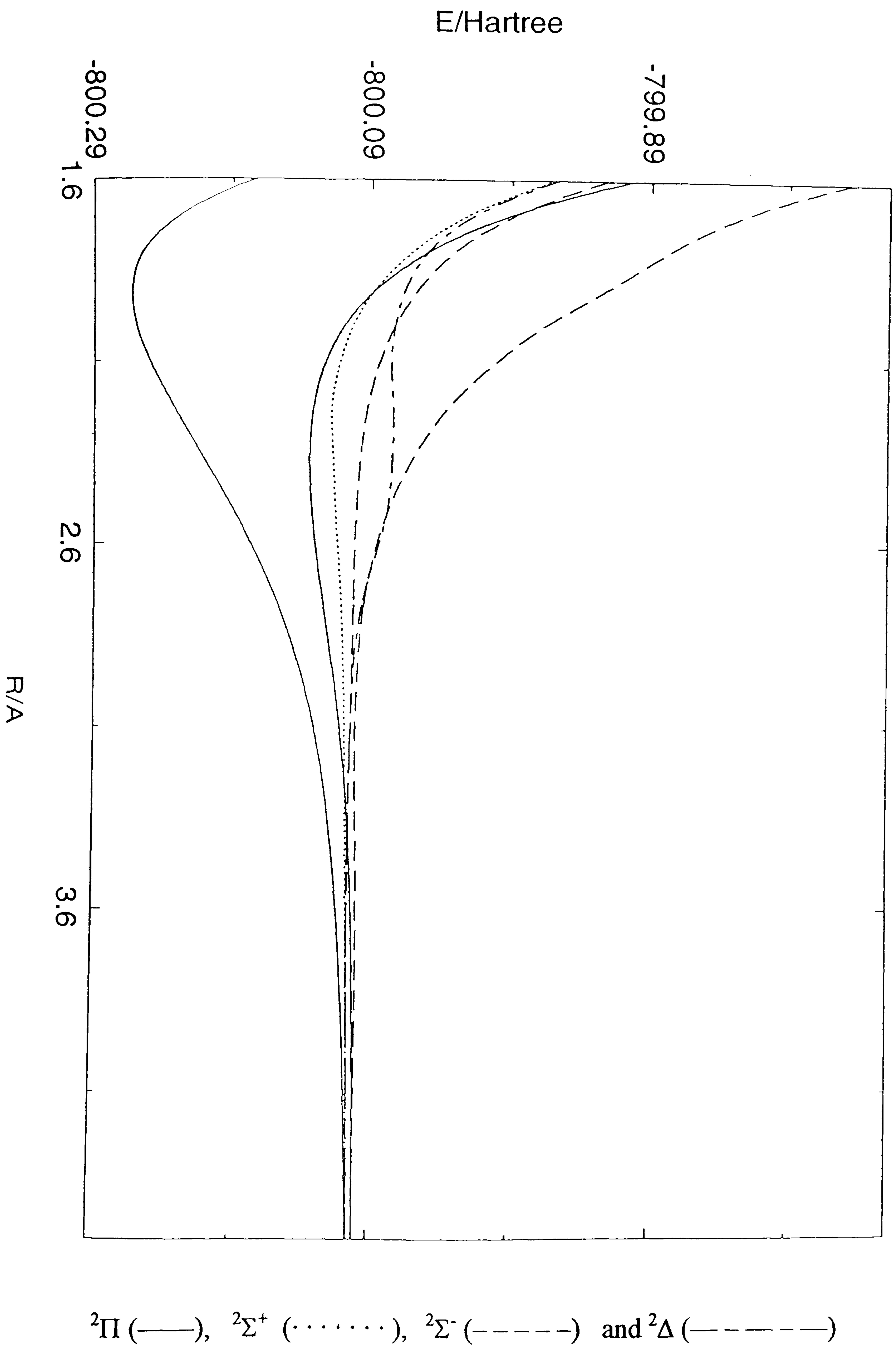


Figure 4.2.10 Calculated potential-energy curves for the quartet states of PCl^+

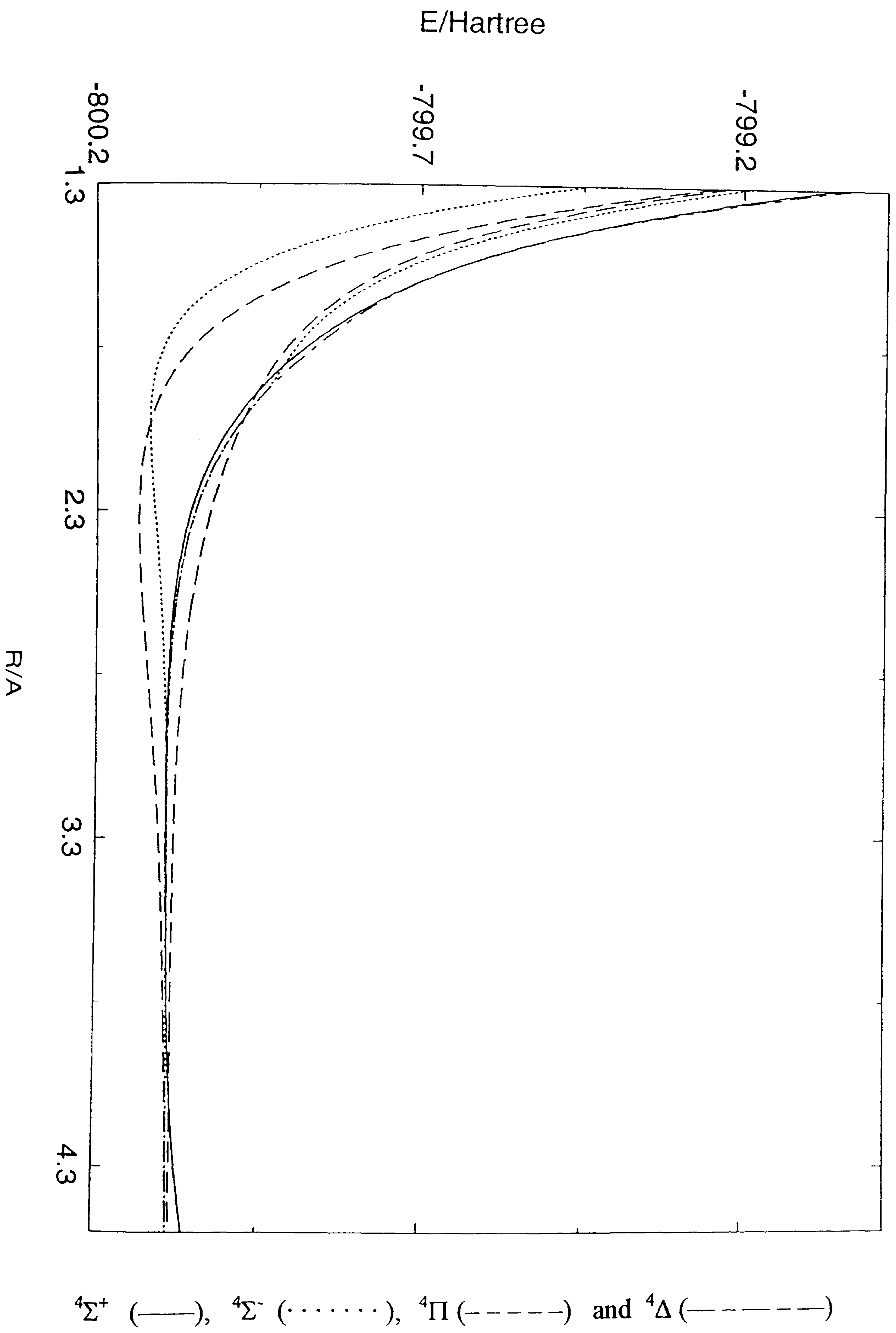


Table 4.1.2.7.A Spectroscopic constants for PCl^+

	$r_e/\text{\AA}$	$E/\text{Hartree}^a$	T_e/eV	μ_e/au^b	ω_e/cm^{-1}	$\omega_{x_e}/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
$X^2\Pi$	1.915	-800.265911	0	-0.748	681.32	2.63	0.279	0.277	0.276	0.280	0.002
	1.900 ^c				689.8 ^d	2.60 ^d				0.284 ^c	0.001 ^c
$A^2\Pi$	2.365	-800.138200	3.475	-0.680	312.81	1.51	0.183	0.181	0.180	0.183	0.001
	2.334 ^c		3.5 ^d		320.6 ^d		0.188 ^c	0.187 ^c			
		(-800.094563)									
$^2\Sigma^+$		-800.093857									
$^2\Delta$		-800.071314									
$1^2\Sigma^-$		-800.063305									
$2^2\Sigma^-$		-799.932182									
$1^4\Pi$	2.325	-800.155260	3.011	-0.413	339.10	3.17	0.189	0.187	0.185	0.189	0.002
		(-800.114834)									
$1^4\Sigma^-$	2.04	-800.138483	3.467	-0.960	427.56	5.98	0.245	0.242	0.238	0.246	0.003
		(-800.134236)									
$2^4\Pi$		-799.969343									
$4\Sigma^+$		-799.965904									
$2^4\Sigma^-$		-799.951790									
4Δ		-799.953006									

^aEnergies in parentheses are vertical energies calculated at $r = 1.915 \text{ \AA}$ for the four bound states mentioned earlier in the discussion.

^bWith respect to the centre of mass and with the direction PCl , $\text{au} = ea_0 \approx 8.4784 \times 10^{-30} \text{ Cm}$.

^cExperimental data [9]. ^dExperimental values [8].

4.1.3 Results for AsCl⁺

This time, unlike NF⁺ and PCl⁺ considered previously, for the two atoms As and Cl we have used different basis sets, namely the density matrix averaged atomic natural orbital (ANO) spd basis set of Pierloot et al. [32]. For all of the calculations we have used the MOLPRO suite of programs [156]. For As this basis set consisted of 17s15p9d basis functions contracted to 9s9p5d and for Cl 13s10p4d functions contracted to 7s7p4d. These basis functions were augmented with the addition of single sets of f functions on As and Cl with exponents $0.5 a_0^{-2}$ and $0.75 a_0^{-2}$ respectively generating a basis set of 123 contracted Gaussian basis functions. As usual, including BBr⁺ which will be discussed in the following section, molecular orbitals for subsequent CI calculations were generated in state averaged CASSCF calculations [146,147] for each spin and symmetry species and the state averaging was carried out over all the states of interest in the CASSCF calculations. The active space comprised the molecular orbitals $11\sigma - 14\sigma$, 5π , 6π . The calculations of the potential energy curves have been performed with the internally contracted CI method of Werner and Knowles [150, 151] where the sets of reference configurations consisted of the configurations used in the CASSCF calculations.

Table 4.3 includes details of the numbers of roots considered (A), the sizes of the reference spaces (B), the numbers of contracted (C) and uncontracted (D) configurations.

Table 4.3 Details of configuration interaction calculations for AsCl⁺

State	A	B	C	D
² Σ ⁺	2	264	220680	7025992
² Π	2	252	220188	6491140
² Σ ⁻	4	240	374960	5948696
⁴ Σ ⁺	4	108	356644	5619904
⁴ Π	2	126	201938	5539026
⁴ Σ ⁻	3	144	280228	5272700

All the energy values and the potential energy curves obtained from the CI calculations using the ANO basis sets [32] with the addition of the f functions for the ²Π, ²Σ⁺, ²Σ⁻, ⁴Σ⁻, ⁴Σ⁺ and ⁴Π states are shown in tables and figures 4.3.1 to 4.3.6, respectively. The dominant configurations obtained from the CI calculations for each of the six states mentioned above are presented in tables 4.1.3.1.A to 4.1.3.6.A respectively. In the region of the equilibrium bond length ($r = 2.055 \text{ \AA}$) for the X²Π state 11σ and 12σ correspond predominantly to a 3s orbital on chlorine and a 4s orbital on arsenic respectively. The orbital 13σ is a bonding orbital and 14σ is an antibonding orbital comprising Cl 3p_σ and As 4p_σ. The orbitals 5π and 6π are bonding and antibonding combinations of p_π orbitals on chlorine and arsenic. As the internuclear distance increases the orbitals 11σ, 13σ and 5π correlate with the 3s, 3p_σ and 3p_π orbitals on chlorine whereas 12σ, 14σ and 6π correlate with the 4s, 4p_σ and 4p_π orbitals on arsenic.

As in previous sections, these calculations have been performed under C_{2v} symmetry and the wavefunctions have been examined and assigned as Σ or Δ.

4.1.3.1 The CI calculations for the $^2\Pi$ states of AsCl^+ with the ANO basis sets [32]

Table 4.3.1, figure 4.3.1 and Table 4.1.3.1.A show, in turn, the energies obtained in the CI calculations, the corresponding potential energy curves and the dominant configurations.

Table 4.1.3.1.A Dominant configurations for the $^2\Pi$ state

State	Configuration	Bond length
$1^2\Pi$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 5\pi^4 6\pi^1$	$r \leq 3.0 \text{ \AA}$
	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 5\pi^3 6\pi^2$	$r \geq 3.1 \text{ \AA}$
$2^2\Pi$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 5\pi^3 6\pi^2$	$r \leq 3.1 \text{ \AA}$
	$\cdots 11\sigma^2 12\sigma^2 13\sigma^1 14\sigma^1 5\pi^4 6\pi^1$	$r \geq 3.2 \text{ \AA}$

As shown in figure 4.3.1, there are bound states from the two potential curves generated. Root1($1^2\Pi$) has a reasonable amount of binding and root2($2^2\Pi$) is weakly bound. Spectroscopic constants for both states have been calculated. Here, also for the two states spectroscopic data have been determined experimentally [33]. Thus, the theoretical and experimental parameters are reported in table 4.1.3.1.B and the calculated constants are compared with experimental data [33] as follows.

Table 4.1.3.1.B Spectroscopic constants for the $^2\Pi$ state

CONSTS	EXPT. ($1^2\Pi$)	ROOT1($1^2\Pi$)	EXPT. ($2^2\Pi$)	ROOT2($2^2\Pi$)
ω_e/cm^{-1}	527.00 ^c	519.42		230.43
$\omega_e x_e/\text{cm}^{-1}$	1.577 ^c	1.69		1.21
B_0/cm^{-1}		0.16738	0.11294 ^c	0.10989
B_1/cm^{-1}		0.16663	0.11217 ^c	0.10911
B_2/cm^{-1}		0.16589		0.10833
B_e/cm^{-1}	0.17140 ^c	0.16775		0.11028
α_e/cm^{-1}	^c 7.68×10^{-4}	7.45×10^{-4}		0.00078
$R_e/\text{\AA}$	2.031 ^c	2.055	2.498 ^c	2.530

^cExperimental data from reference [33].

In the case of the $1^2\Pi$ state, the errors between ω_e , $\omega_e x_e$, B_e , α_e and R_e , and experimental values [33] are 1.44 %, 7.17 %, 2.13 %, 2.99 % and 1.18 %.

For the $2^2\Pi$ state, there are errors of 2.70 %, 2.73 % and 1.28 % between the theoretical values of B_0 , B_1 , and R_e , and the experimental parameters. Therefore, for both states there is reasonable agreement with experiment.

4.1.3.2 The CI calculations for the $^2\Sigma^+$ state of AsCl^+ with the ANO basis sets [32]

The energies obtained, the potential energy curves and the dominant configurations are in table 4.3.2, figure 4.3.2 and table 4.1.3.1.A respectively. The wavefunctions have been examined and assigned as Σ^+ or Δ . Roots 1 and 2 are, in turn, a $^2\Sigma^+$ state and a $^2\Delta$ state.

Table 4.1.3.2.A Dominant configurations for the $^2\Sigma^+$ state

State	Configuration	Bond length
$^2\Sigma^+$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 14\sigma^1 5\pi^4$	$r \leq 2.8 \text{ \AA}$
	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 14\sigma^1 5\pi^3 6\pi^1$	$r \geq 2.9 \text{ \AA}$
$^2\Delta$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^1 5\pi^4 6\pi^2$	$r \leq 2.4 \text{ \AA}$
	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 14\sigma^1 5\pi^3 6\pi^1$	$r \geq 2.5 \text{ \AA}$

From the figure 4.3.2 it can be seen that there are no bound states. State 1 has a very shallow minimum and state 2 is repulsive. For these two states no theoretical spectroscopic constants have been computed and no experimental data are available.

4.1.3.3 The CI calculations for the $^2\Sigma^-$ states of AsCl^+ with the ANO basis sets [32]

We encountered the same problem as in NF^+ and PCl^+ . To avoid convergence problems we have calculated 4 states rather than the 3 states correlating with the combination of $\text{Cl}(^2\text{P}) + \text{As}^+(^3\text{P})$ as shown in figure 3. Thus, the first three roots

have been selected, examined and assigned as Σ^- or Δ . The energies of the four states at each bond length, the three corresponding potential energy curves and the dominant configurations are given in table 4.3.3, figure 4.3.3 and table 4.1.3.3.A respectively. Roots 1 and 3 are $^2\Sigma^-$ states and root2 is a $^2\Delta$ state.

Table 4.1.3.3.A Dominant configurations for the $^2\Sigma^-$ state

State	Configuration	Bond length
$1^2\Sigma^-$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^1 5\pi^4 6\pi^2$	
$2^2\Sigma^-$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^1 5\pi^3 6\pi^3$	$r \leq 1.8 \text{ \AA}$
	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 14\sigma^1 5\pi^3 6\pi^1$	$r \geq 1.9 \text{ \AA}$

For the $^2\Delta$ state the dominant configurations are as given in Table 4.1.3.2.A. From figure 4.3.3 the three roots are seen to be repulsive. Thus, no theoretical constants have been calculated. In addition, no experimental data are available.

4.1.3.4 The CI calculations for the $^4\Sigma^-$ states of AsCl^+ with the ANO basis sets [32]

Table 4.3.4, figure 4.3.4 and table 4.1.3.4.A show, in turn, the energies, the potential curves and the dominant configurations. Roots 1 and 2 are $^4\Sigma^-$ states and root3 is a $^4\Delta$ state.

Table 4.1.3.4.A Dominant configurations for the $^4\Sigma^-$ states

State	Configuration	Bond length
$1^4\Sigma^-$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^1 5\pi^4 6\pi^2$	
$2^4\Sigma^-$	$\cdots 11\sigma^2 12\sigma^1 13\sigma^2 5\pi^4 6\pi^2$	$r \leq 1.9 \text{ \AA}$
	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 14\sigma^1 5\pi^3 6\pi^1$	$r \geq 2.0 \text{ \AA}$
$^4\Delta$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^1 5\pi^3 6\pi^3$	$r \leq 1.8 \text{ \AA}$
	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 14\sigma^1 5\pi^3 6\pi^1$	$r \geq 1.8 \text{ \AA}$

Figure 4.3.4 shows that root1 is a bound state and roots 2 and 3 are repulsive. Thus, theoretical spectroscopic constants have calculated for the $1^4\Sigma^-$ state and are given in table 4.1.3.4.B.

Table 4.1.3.4.B Spectroscopic constants of the $1^4\Sigma^-$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$1^4\Sigma^-$	227.60	4.62	0.1367	0.1342	0.2632	0.1380	0.0025	2.265

Since no experimental data are available for the $^4\Sigma^-$ state, the theoretical spectroscopic constants of the $1^4\Sigma^-$ state can be predictive of experimental parameters.

4.1.3.5 The CI calculations for the $^4\Sigma^+$ states of AsCl^+ with the ANO basis sets[32]

Due to convergence problems we have also considered 4 states rather than 2 states and the first two roots have been chosen, examined and labelled as Σ^+ or Δ . Table 4.3.5, figure 4.3.5 and table 4.1.3.5.A present, in turn, the energy values, the potential curves and the dominant configurations. Roots 1 and 2 is a $^4\Sigma^+$ state and a $^4\Delta$ state.

Table 4.1.3.5.A Dominant configurations for the $^4\Sigma^+$ state

State	Configuration	Bond length
$^4\Sigma^+$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 14\sigma^1 5\pi^3 6\pi^1$	

For the $^4\Delta$ state the dominant wavefunctions are given in the previous subsection.

Because states 1 and 2 are repulsive no theoretical constants have been obtained. On the other hand, for these states no experimental parameters have been determined.

4.1.3.6 The CI calculations for the $^4\Pi$ states of AsCl^+ with the ANO basis sets [32]

The energies, the potential curves and the dominant configurations are in table 4.3.6, figure 4.3.6 and table 4.1.3.6.A respectively.

Table 4.1.3.6.A Dominant configurations for the ${}^4\Pi$ state

State	Configuration	Bond length
$1^4\Pi$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^2 5\pi^3 6\pi^2$	
$2^4\Pi$	$\cdots 11\sigma^2 12\sigma^2 13\sigma^1 14\sigma^1 5\pi^4 6\pi^1$	

The $1^4\Pi$ state is bound and the calculated spectroscopic constants are reported in table 4.1.3.6.B whereas the $2^4\Pi$ state is repulsive.

Table 4.1.3.6.B Spectroscopic constants of the $1^4\Pi$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$1^4\Pi$	247.56	1.48	0.1130	0.1122	0.1114	0.1134	0.0008	2.480

There are no experimental data available for comparison with our theoretical values.

4.1.3.7 General discussion for AsCl^+

For the doublet and quartet states the calculated potential energy curves are shown in figures 4.3.9 and 4.3.10 respectively. As in the case of NF^+ and PCl^+ , it can be seen from the two figures that there are four bound states, namely $1^2\Pi$, $2^2\Pi$, $1^4\Sigma^-$ and $1^4\Pi$.

The $1^2\Pi$ state is the ground state, $X^2\Pi$, which has an equilibrium bond length of $r = 2.055 \text{ \AA}$ and the $2^2\Pi$ state is the second root, $A^2\Pi$, which has a shallow minimum at the bond length of 2.530 \AA . The ${}^2\Sigma^+$ state has a very shallow minimum and for the ${}^2\Delta$ state in the region of $r = 2.5 \text{ \AA}$ the shoulder in the potential energy curve arises from an avoided crossing with a higher ${}^2\Delta$ state. In this region the dominant configuration changes from $\cdots 11\sigma^2 12\sigma^2 13\sigma^1 5\pi^4 6\pi^2$ to $\cdots 11\sigma^2 12\sigma^2 13\sigma^2 14\sigma^1 5\pi^3 6\pi^1$ as the

bond length is increased. There are several points in common between AsCl^+ and PCl^+ . First, the potential energy curves of the excited states of AsCl^+ are similar to those for PCl^+ . For these two species the four bound states mentioned above are the same. Second, as in the case of PCl^+ , the hump on the $^2\Delta$ potential curve in the region of $r = 2.5 \text{ \AA}$ arises from an avoided intersection with a higher $^2\Delta$ state. For the $2^2\Sigma^-$ state, the dominant wavefunction changes in the vicinity of $r = 1.8 \text{ \AA}$ but this is not apparent from the potential energy curve. Third, for the $1^4\Sigma^-$ and $1^4\Pi$ states there are significant differences in the equilibrium bond lengths. Thus, for this transition the Franck-Condon factors are expected to be unfavourable. The bound states of the quartet states for AsCl^+ are similar to those for NF^+ , PF^+ and PCl^+ . Table 4.1.3.7.A presents the theoretical spectroscopic constants, T_e values, dipole moments for the bound states and the vertical energies of all the states calculated at the equilibrium bond length of $r = 2.055 \text{ \AA}$ for the $X^2\Pi$ state. As described earlier in the subsection 4.1.3.1, for the $X^2\Pi$ state the theoretical constants for ω_e , $\omega_e x_e$ and R_e are in good agreement with the experimental parameters from Coxon et. al. [33] and for the $A^2\Pi$ state the agreement for the calculated constant for B_0 is comparable with that for the $X^2\Pi$ state. No experimental parameters are available for ω_e and $\omega_e x_e$ for the $A^2\Pi$ state, but from the T_1 and T_0 values of Coxon et. al. [33] a value of $\Delta G_{1/2}$ of 232.2 cm^{-1} has been derived for the separation of the $\nu = 0$ and $\nu = 1$ levels which compares well with the value of 228.0 cm^{-1} obtained from the theoretical constants ω_e and $\omega_e x_e$.

In our work we have not considered the effect of spin-orbit coupling.

For the $A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$ transition the experimental data from Coxon et.al [31] have been determined. They mention that the spin-orbit coupling is approximately 1387 cm^{-1} for the X state and in the range $100 - 200\text{ cm}^{-1}$ for the A state. Inclusion of spin-orbit coupling would have an effect on the theoretical T_e values but the effect on the vibrational and rotational constants is expected to be much smaller. Liebeman et.al [159] made relativistic CI calculations for the AsF molecule. In the case of the $A^3\Pi$ state consideration of spin-orbit coupling causes a splitting of about 1400 cm^{-1} between the highest and lowest multiplets but the differences in the r_e and ω_e constants are much smaller. A recent paper of Latifzadeh and Balasubramanian [56] presents calculations for the potential energy curves for AsF using relativistic core potentials. However, in their calculations the effects of spin-orbit coupling have not been considered. Dipole moments and dipole moment functions for the bound states mentioned earlier are given in table 4.3.7 and figure 4.3.7. For a molecular ion the dipole moment depends on the origin selected. Dipole moments have been computed with respect to the centre of mass and in the direction AsCl. As the bond length increases the ion dissociate to $\text{As}^+ + \text{Cl}$, the calculated dipole moments continuously decrease and should approach a monotonically decreasing function of r . The electronic transition moments and the electronic transition moment functions for the $A^2\Pi \rightarrow X^2\Pi$ and $1^4\Sigma^- \rightarrow 1^4\Pi$ transitions are given in table 4.3.8 and figure 4.3.8. Due to the difference in the equilibrium bond length for the two quartet bound states electronic transitions are unlikely.

At the end of the previous subsection 4.1.2.7, we have described that the spacing of the electronic states decreases as we move down from the first to the second row of

the periodic table due to the effect of additional inner shell electrons. This trend is continued on moving to the third row with T_e values 5.1, 4.5, 3.5 and 3.1 eV for the A state for NF^+ , PF^+ , PCl^+ and AsCl^+ respectively. In addition, the depth of the well, which is approximately a value of 3.4 eV for the $\text{X}^2\Pi$ state of AsCl^+ , is considerably less than the value of 4.3 eV for PCl^+ .

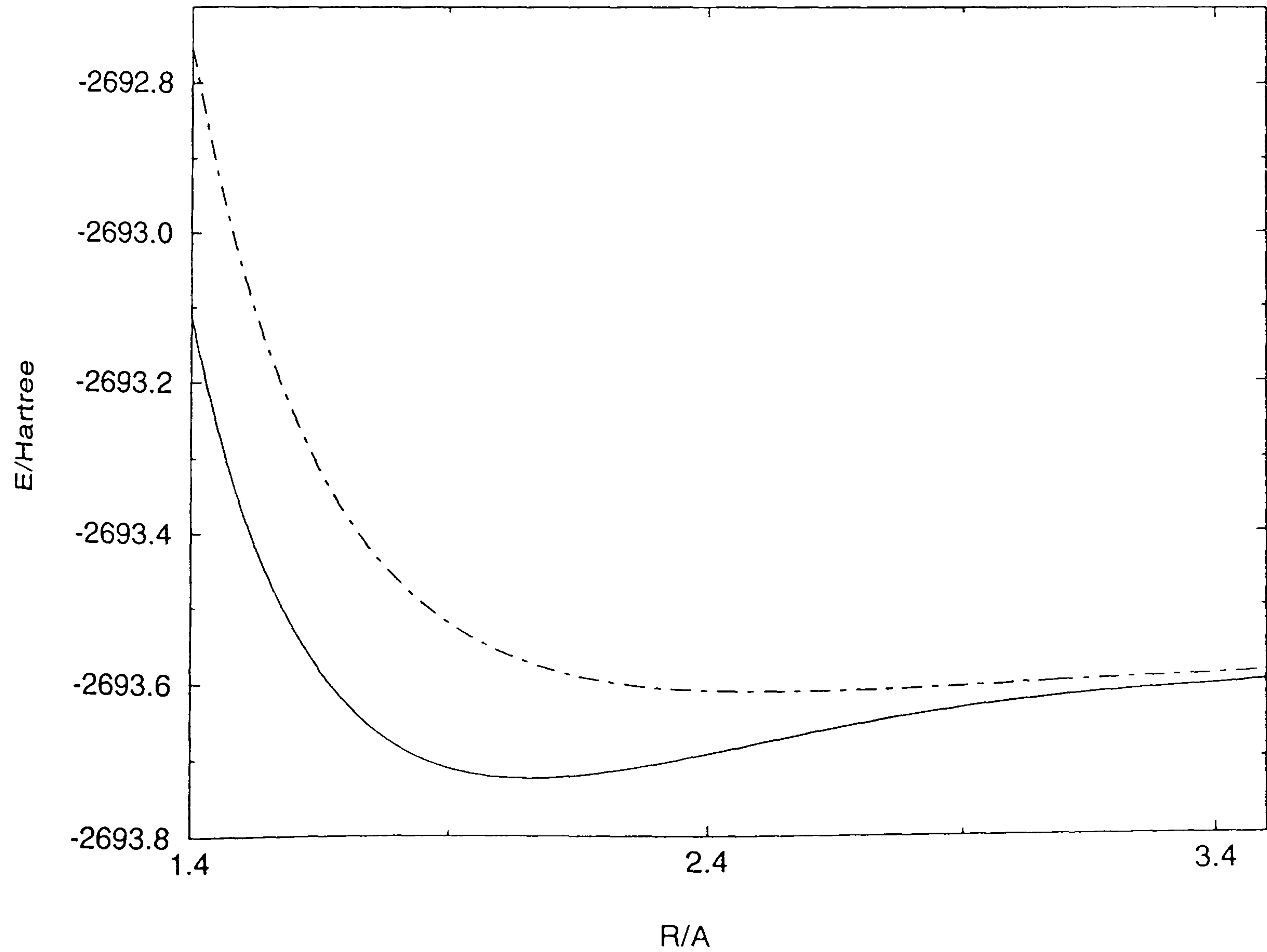
From the comparison of our spectroscopic constants with the experimental data for the $\text{X}^2\Pi$ and $\text{A}^2\Pi$ states it is believed that calculations at this level can provide a reasonable description of potential energy curves for molecules which include elements from the third row of the periodic table.

4.3.1 The CI results for the $^2\Pi$ states of AsCl^+ with the ANO basis sets [32]

Table 4.3.1 Theoretical energy values		
R/Å	ROOT1	ROOT2
1.4	-2693.122789	-2692.762089
1.5	-2693.376793	-2693.055177
1.6	-2693.537014	-2693.251686
1.7	-2693.634909	-2693.383030
1.8	-2693.691644	-2693.470648
1.9	-2693.721106	-2693.528795
2.0	-2693.732876	-2693.566899
2.1	-2693.733321	-2693.591392
2.2	-2693.726746	-2693.606627
2.3	-2693.716073	-2693.615554
2.4	-2693.703295	-2693.620182
2.5	-2693.689781	-2693.621887
2.6	-2693.676469	-2693.621621
2.7	-2693.663999	-2693.620050
2.8	-2693.652786	-2693.617653
2.9	-2693.643060	-2693.614787
3.0	-2693.634884	-2693.611730
3.1	-2693.628162	-2693.608703
3.2	-2693.622669	-2693.605860
3.3	-2693.618086	-2693.603237
3.5	-2693.608130	-2693.596105
4.0	-2693.546490	-2693.539144
4.5	-2693.543242	-2693.538461
5.0	-2693.541700	-2693.538434

E/Hartree

Figure 4.3.1 Calculated potential energy curves



4.3.2 The CI results for the $^2\Sigma^+$ states of AsCl^+ with the ANO basis sets [32]

Table 4.3.2 Theoretical energy values

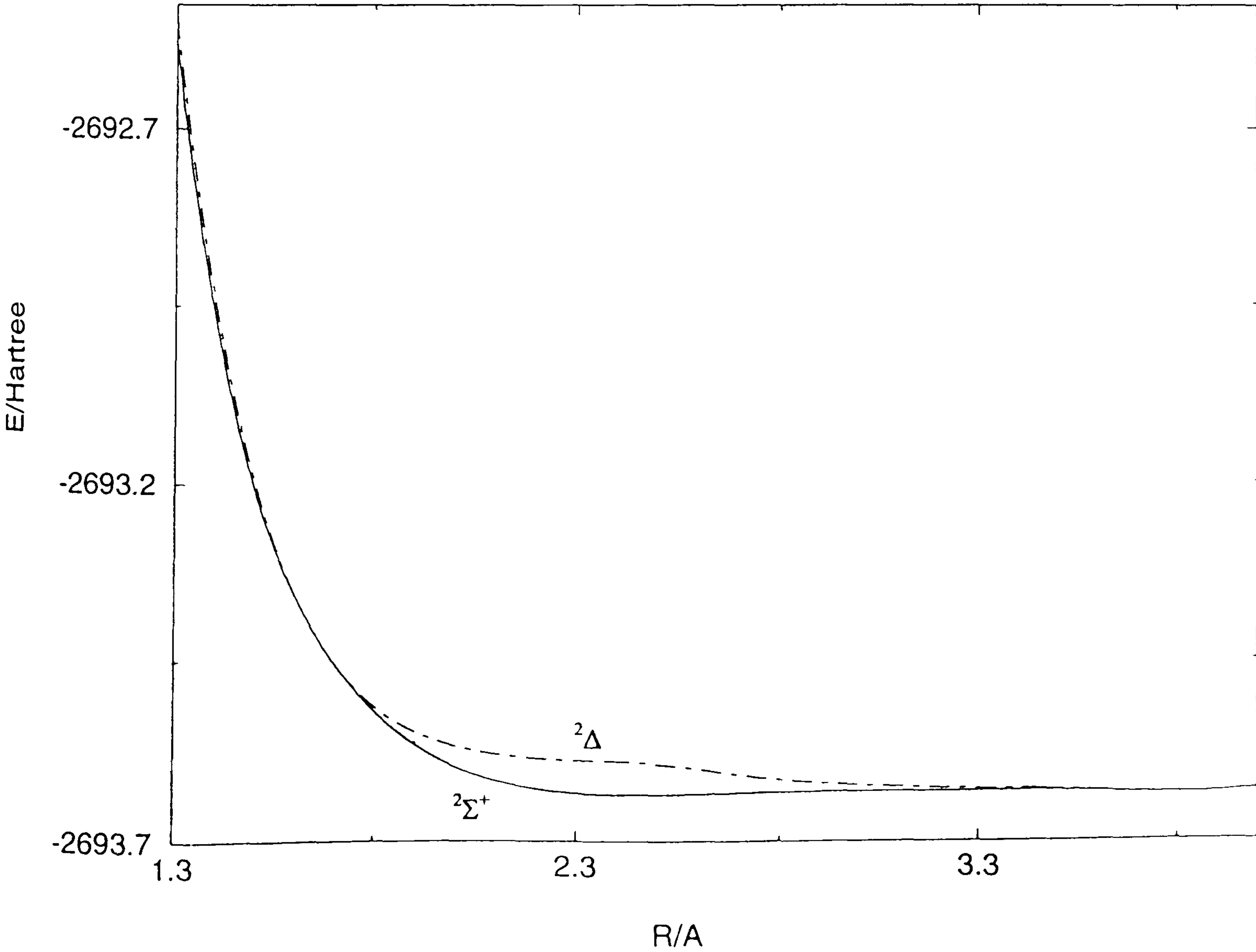
R/Å	ROOT1	ROOT2
1.3	-2692.547378	-2692.518111
1.4	-2692.930073	-2692.907615
1.5	-2693.172638	-2693.160484
1.6	-2693.323760	-2693.321897
1.7	-2693.422379	-2693.423172
1.8	-2693.490328	-2693.484148
1.9	-2693.536960	-2693.519760
2.0	-2693.567965	-2693.539946
2.1	-2693.587573	-2693.551065
2.2	-2693.599108	-2693.557020
2.3	-2693.605082	-2693.560082
2.4	-2693.607392	-2693.561529
2.6	-2693.606832	-2693.572329
2.7	-2693.605482	-2693.580893
2.8	-2693.604339	-2693.587184
2.9	-2693.603588	-2693.591759
3.0	-2693.603191	-2693.595044
3.3	-2693.602877	-2693.600059
3.5	-2693.602669	-2693.601180
4.0	-2693.601494	-2693.601096
4.5	-2693.541293	-2693.541139
5.0	-2693.539184	-2693.539103

$^2\Sigma^+$

$^2\Delta$

E/Hartree

Figure 4.3.2 Calculated potential energy curves



4.3.3 The CI results for the $^2\Sigma^-$ states of AsCl^+ with the ANO basis sets [32]

Table 4.3.3 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4
1.6	-2693.292760	-2693.324424	-2693.092987	-2693.098662
1.7	-2693.398709	-2693.424770	-2693.214996	-2693.214845
1.8	-2693.466571	-2693.484959	-2693.294657	-2693.292330
1.9	-2693.510196	-2693.519877	-2693.355341	-2693.354167
2.0	-2693.539180	-2693.540167	-2693.414788	-2693.413258
2.1	-2693.558486	-2693.551406	-2693.460490	-2693.461830
2.2	-2693.571403	-2693.557406	-2693.496495	-2693.497799
2.3	-2693.580065	-2693.560463	-2693.523744	-2693.525049
2.4	-2693.585869	-2693.561883	-2693.544268	-2693.545537
2.5	-2693.589745	-2693.562994	-2693.559648	-2693.560223
2.6	-2693.592327	-2693.572617	-2693.571106	-2693.561935
2.7	-2693.594048	-2693.581023	-2693.579576	-2693.561621
2.8	-2693.595215	-2693.587230	-2693.585762	-2693.561178
2.9	-2693.596075	-2693.591771	-2693.590171	-2693.560814
3.0	-2693.596882	-2693.595098	-2693.593087	-2693.560847
3.1	-2693.597921	-2693.597455	-2693.594494	-2693.561439
3.2	-2693.599017	-2693.598986	-2693.594993	-2693.561822
3.3	-2693.599743	-2693.599864	-2693.595048	-2693.561854

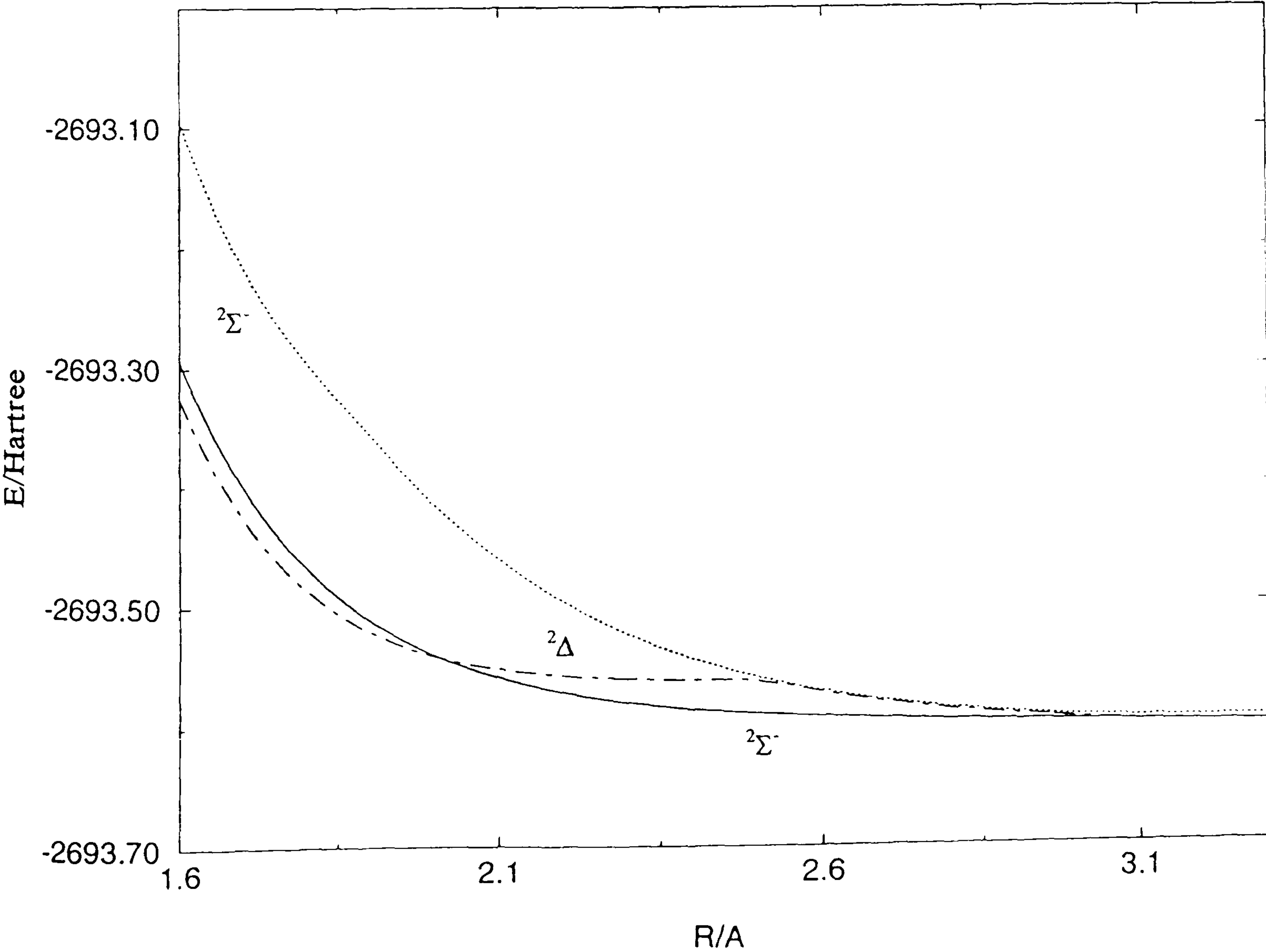
$^2\Sigma^-$

$^2\Delta$

$^2\Sigma^-$

E/Hartree

Figure 4.3.3 Calculated potential energy curves

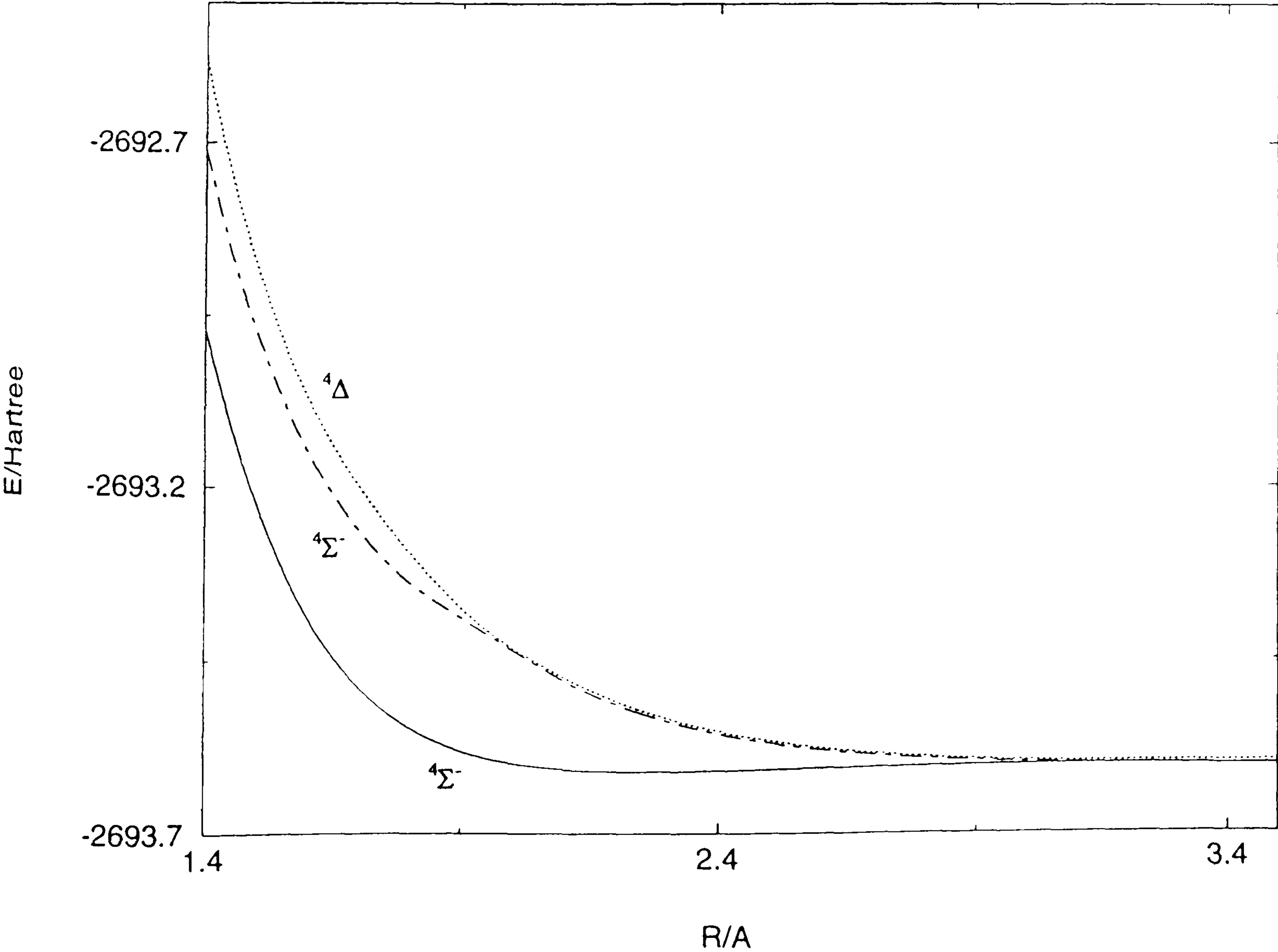


4.3.4 The CI results for the $^4\Sigma^-$ states of AsCl^+ with the ANO basis sets [32]

Table 4.3.4 Theoretical energy values			
R/Å	ROOT1	ROOT2	ROOT3
1.4	-2692.971738	-2692.712195	-2692.584304
1.5	-2693.226264	-2692.974640	-2692.875809
1.6	-2693.388252	-2693.147789	-2693.069931
1.7	-2693.488755	-2693.261918	-2693.197731
1.8	-2693.547355	-2693.337159	-2693.293873
1.9	-2693.581797	-2693.387162	-2693.373188
2.0	-2693.599794	-2693.434133	-2693.430915
2.1	-2693.608400	-2693.479754	-2693.474448
2.2	-2693.611528	-2693.513797	-2693.508660
2.3	-2693.611835	-2693.539090	-2693.534458
2.4	-2693.610839	-2693.557755	-2693.553665
2.5	-2693.609329	-2693.571409	-2693.567814
2.6	-2693.607689	-2693.581296	-2693.578117
2.7	-2693.606109	-2693.588368	-2693.585513
2.8	-2693.604689	-2693.593356	-2693.590713
2.9	-2693.603503	-2693.596811	-2693.594240
3.0	-2693.602644	-2693.599149	-2693.596440
3.1	-2693.602214	-2693.600679	-2693.597531
3.2	-2693.602178	-2693.601631	-2693.597780
3.3	-2693.602292	-2693.602172	-2693.597593
3.5	-2693.602437	-2693.602305	-2693.596919
	$^4\Sigma^-$	$^4\Sigma^-$	$^4\Delta$

E/Hartree

Figure 4.3.4 Calculated potential energy curves



4.3.5 The CI results for the $^4\Sigma^+$ states of AsCl^+ with the ANO basis sets [32]

Table 4.3.5 Theoretical energy values

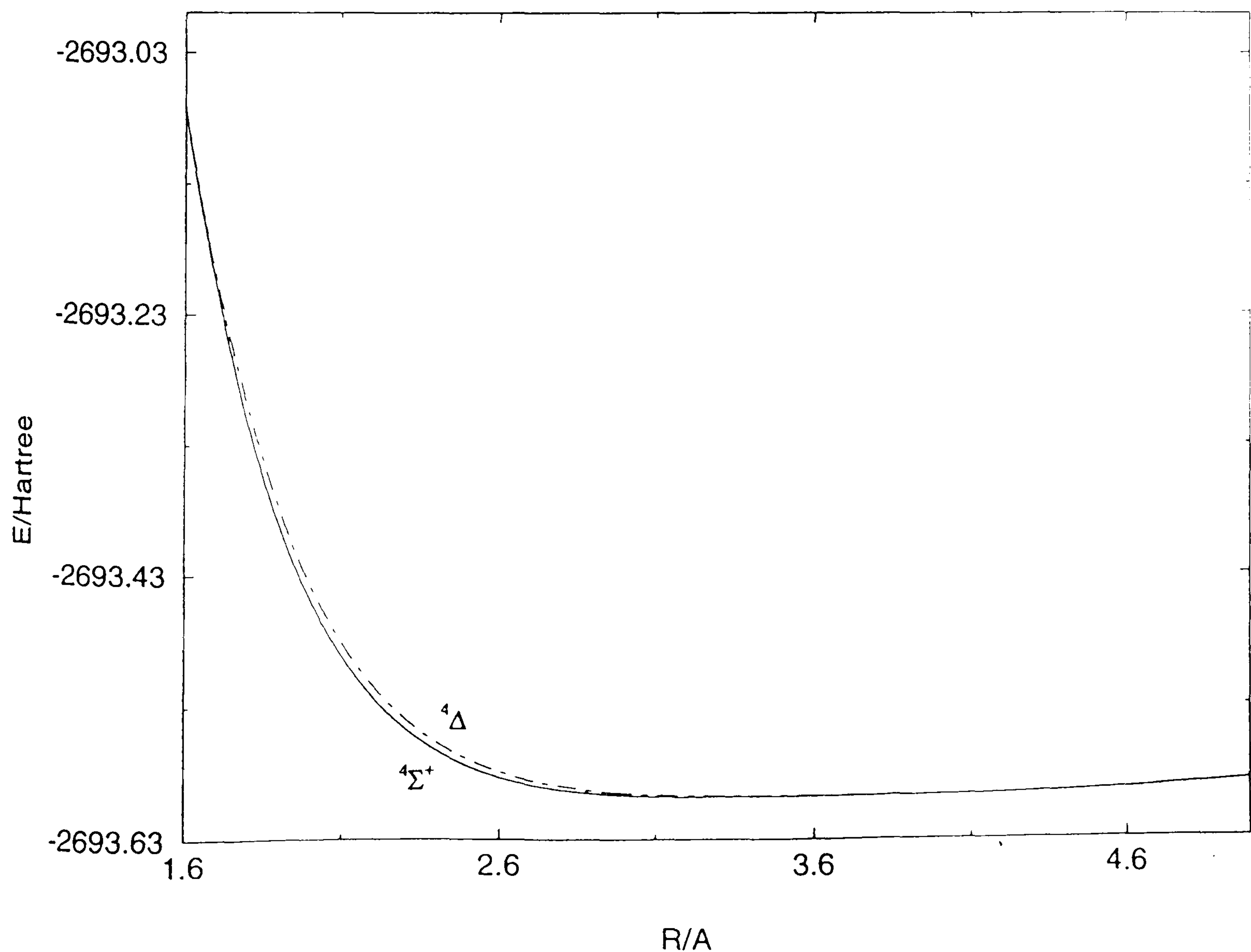
R/Å	ROOT1	ROOT2	ROOT3	ROOT4
1.6	-2693.072407	-2693.069057	-2693.058171	-2693.048538
1.7	-2693.206890	-2693.201020	-2693.186039	-2693.179955
1.8	-2693.309713	-2693.296478	-2693.275369	-2693.272852
1.9	-2693.387998	-2693.374571	-2693.331318	-2693.327368
2.0	-2693.446518	-2693.434569	-2693.364493	-2693.360774
2.1	-2693.489967	-2693.479636	-2693.383894	-2693.380599
2.2	-2693.522032	-2693.513228	-2693.394766	-2693.391903
2.3	-2693.545487	-2693.538056	-2693.400630	-2693.398176
2.4	-2693.562426	-2693.556200	-2693.403865	-2693.401836
2.5	-2693.574435	-2693.569136	-2693.414028	-2693.405701
2.6	-2693.582965	-2693.578579	-2693.433472	-2693.407728
2.7	-2693.588815	-2693.585202	-2693.448490	-2693.410185
2.8	-2693.592432	-2693.589474	-2693.459988	-2693.411991
2.9	-2693.595067	-2693.592685	-2693.468628	-2693.417810
3.0	-2693.596720	-2693.594797	-2693.475113	-2693.423326
3.1	-2693.597644	-2693.596089	-2693.479912	-2693.427394
3.2	-2693.598083	-2693.596823	-2693.483439	-2693.430346
3.3	-2693.598215	-2693.597192	-2693.486016	-2693.432467
3.5	-2693.598075	-2693.597391	-2693.489298	-2693.435113
4.0	-2693.596973	-2693.596692	-2693.491907	-2693.437085
4.5	-2693.593772	-2693.593629	-2693.489736	-2693.434735
5.0	-2693.586729	-2693.586647	-2693.483330	-2693.428209

$^4\Sigma^+$

$^4\Delta$

E/Hartree

Figure 4.3.5 Calculated potential energy curves



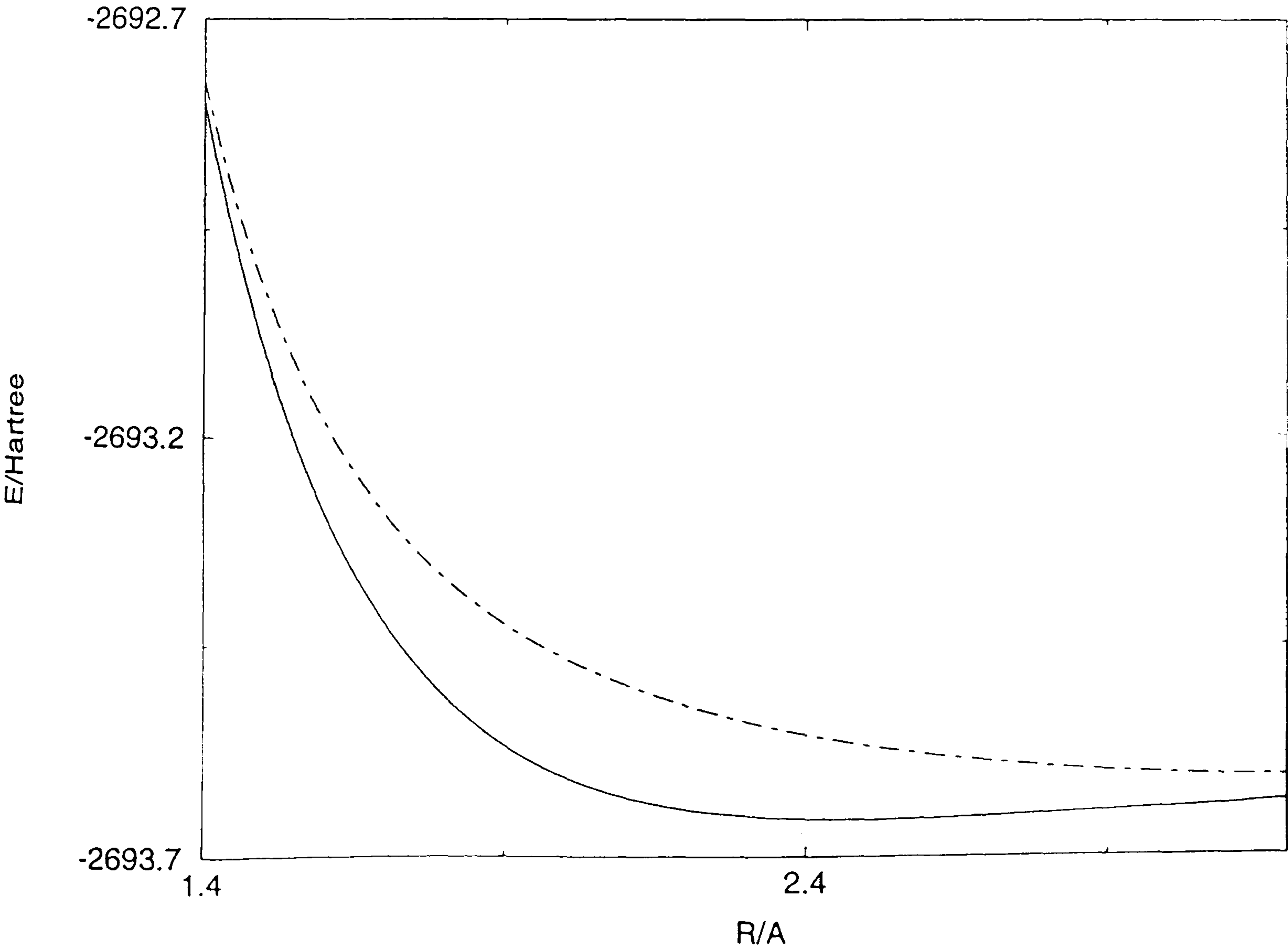
4.3.6 The CI results for the $^4\Pi$ states of AsCl^+ with the ANO basis sets [32]

Table 4.3.6 Theoretical energy values

R/Å	ROOT1	ROOT2
1.4	-2692.776906	-2692.750956
1.5	-2693.071151	-2692.998238
1.6	-2693.269061	-2693.160016
1.7	-2693.401652	-2693.270117
1.8	-2693.489951	-2693.347630
1.9	-2693.548201	-2693.403464
2.0	-2693.586032	-2693.444698
2.1	-2693.609957	-2693.476070
2.2	-2693.624397	-2693.500635
2.3	-2693.632380	-2693.520267
2.4	-2693.636006	-2693.536108
2.5	-2693.636741	-2693.548908
2.6	-2693.635611	-2693.559210
2.7	-2693.633334	-2693.567443
2.8	-2693.630408	-2693.573963
2.9	-2693.627169	-2693.579061
3.0	-2693.623824	-2693.582965
3.1	-2693.620398	-2693.585761
3.2	-2693.615894	-2693.586534

E/Hartree

Figure 4.3.6 Calculated potential energy curves



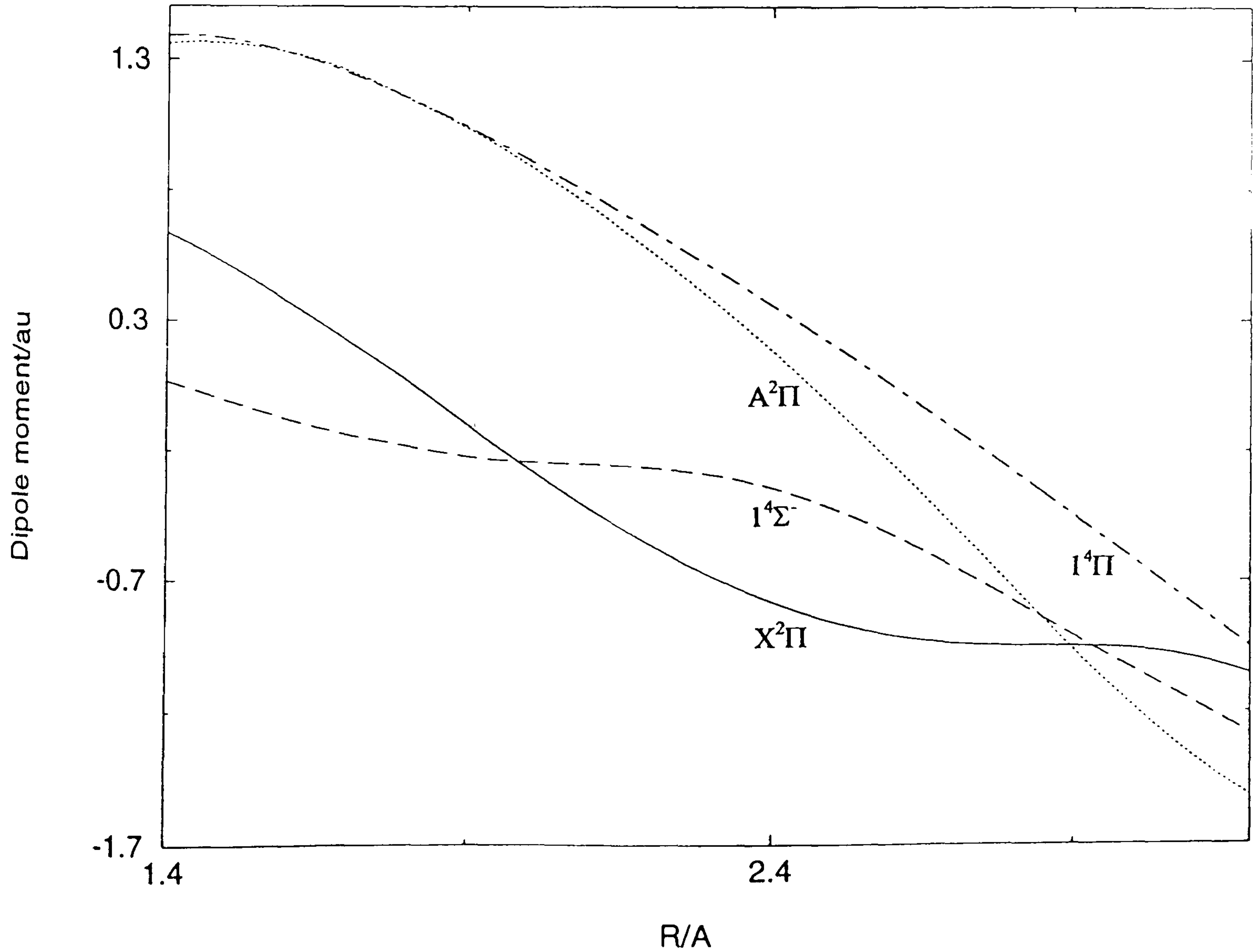
4.3.7 Dipole moments for the bound states of AsCl⁺

Table 4.3.7 Dipole moment values

R/Å	X ² Π	A ² Π	1 ⁴ Σ ⁻	1 ⁴ Π
1.5	0.5192	1.3598	-0.0055	1.3770
1.6	0.3781	1.3274	-0.0750	1.3271
1.7	0.2265	1.2594	-0.1342	1.2518
1.8	0.0739	1.1554	-0.1773	1.1559
1.9	-0.0961	1.0374	-0.2189	1.0439
2.0	-0.2627	0.8990	-0.2399	0.9200
2.1	-0.4191	0.7427	-0.2511	0.7877
2.2	-0.5603	0.5702	-0.2651	0.6495
2.3	-0.6822	0.3830	-0.2940	0.5062
2.4	-0.7820	0.1818	-0.3469	0.3580
2.5	-0.8576	-0.0323	-0.4263	0.2049
2.6	-0.9085	-0.2578	-0.5289	0.0469
2.7	-0.9361	-0.4919	-0.6483	-0.1155
2.8	-0.9456	-0.7295	-0.7769	-0.2814
2.9	-0.9473	-0.9622	-0.9077	-0.4494
3.0	-0.9568	-1.1778	-1.0352	-0.6177
3.1	-0.9895	-1.3641	-1.1579	-0.7844
3.2	-1.0539	-1.5159	-1.2801	-0.9487

Dipole moment/au

Figure 4.3.7 Electronic dipole moment functions



4.3.8 Electronic transition moments for AsCl⁺

Table 4.3.8 Transition moment values

R/Å	A ² Π → X ² Π	1 ⁴ Σ ⁻ → 1 ⁴ Π
1.5	0.0327	-0.2350
1.6	0.0527	-0.2317
1.7	0.0893	-0.2232
1.8	0.1270	-0.2106
1.9	0.1725	-0.1944
2.0	0.2254	-0.1756
2.1	0.2840	-0.1551
2.2	0.3458	-0.1336
2.3	0.4074	-0.1122
2.4	0.4645	-0.0920
2.5	0.5083	-0.0735
2.6	0.5407	-0.0571
2.7	0.5546	-0.0428
2.8	0.5452	-0.0305
2.9	0.5092	-0.0194
3.0	0.4472	-0.0091

Electronic transition moment/au

Figure 4.3.8 Electronic transition moments

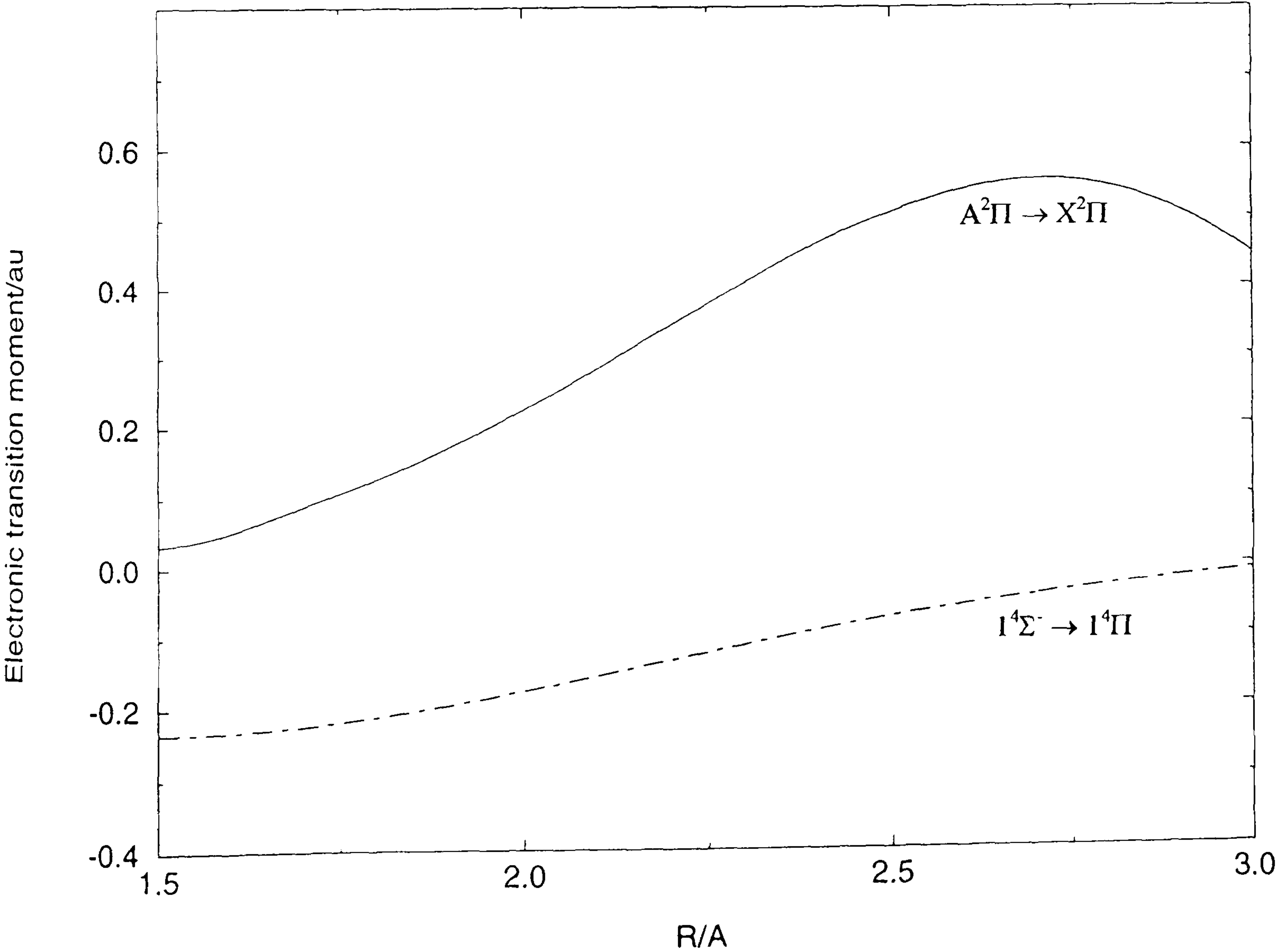


Figure 4.3.9 Calculated potential-energy curves for the doublet states of AsCl^+

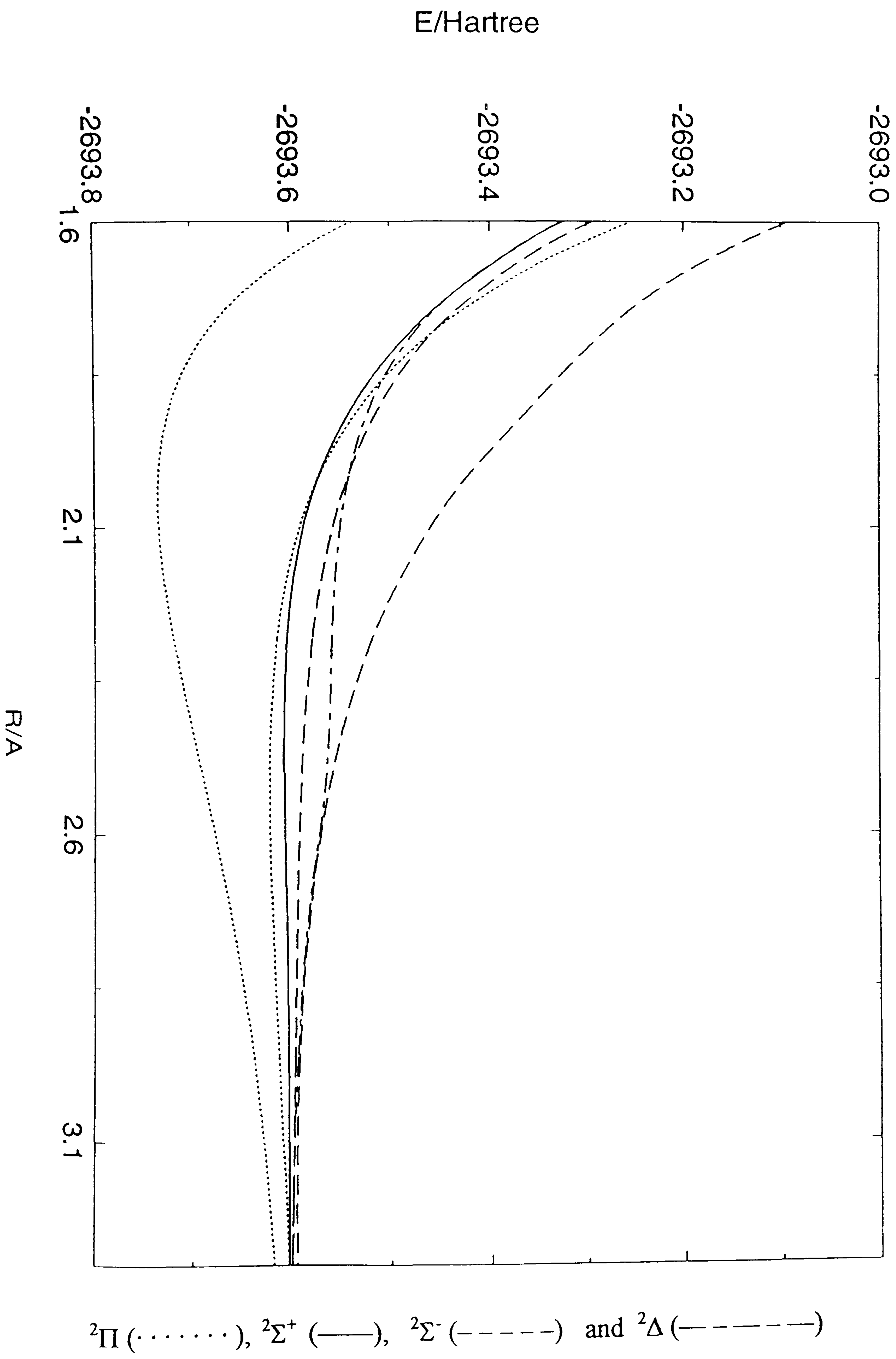


Figure 4.3.10 Calculated potential-energy curves for the quartet states of AsCl^+

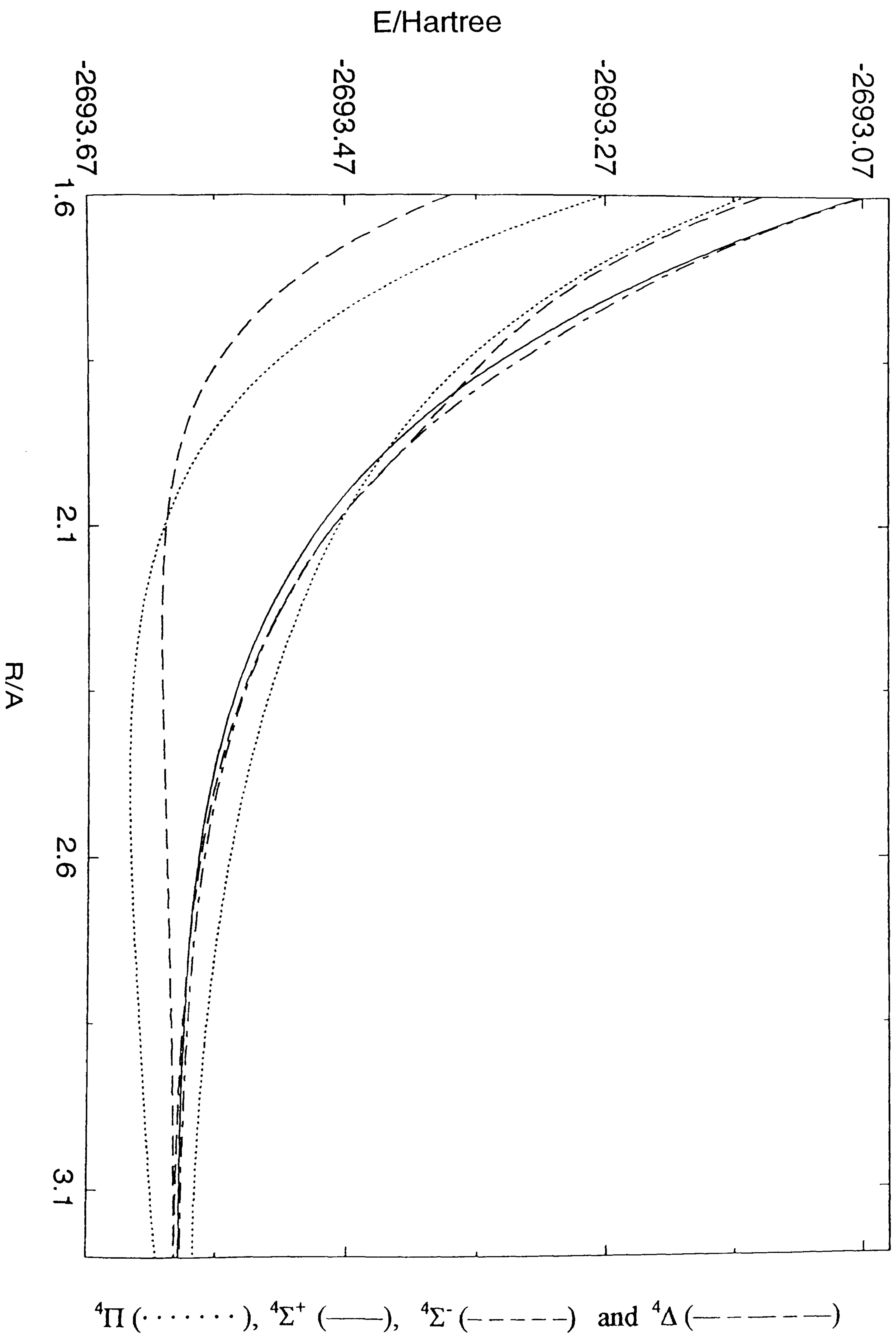


Table 4.1.3.7.A Spectroscopic constants for AsCl⁺

	$r_e/\text{\AA}$	$E/\text{Hartree}^a$	T_e/eV	μ_e/au^b	ω_e/cm^{-1}	$\omega_{x_e}/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_3/cm^{-1}	α_e/cm^{-1}
X ² Π	2.055	-2693.734208	0	-0.3504	519.42	1.69	0.16738	0.16663	0.16589	0.16775	0.00074
	2.031 ^c				527.00	1.577				0.17140	0.00077
A ² Π	2.530	-2693.621979	3.054	-0.0989	230.43	1.21	0.10989	0.10911	0.10833	0.11028	0.00078
	2.498 ^c		3.26 ^c				0.11294	0.11217			
		(-2693.581737)									
² Σ ⁺		-2693.579926									
1 ² Σ ⁻		-2693.550754									
² Δ		-2693.546888									
2 ² Σ ⁻		-2693.440778									
1 ⁴ Π	2.480	-2693.636771	2.651	0.2359	247.56	1.48	0.11299	0.11218	0.11136	0.11341	0.00082
		(-2693.600590)									
1 ⁴ Σ ⁻	2.265	-2693.611934	3.327	-0.2815	227.60	4.62	0.13671	0.13417	0.26324	0.13798	0.00254
		(-2693.605406)									
⁴ Σ ⁺		-2693.472020									
⁴ Δ		-2693.460975									
2 ⁴ Π		-2693.462945									
2 ⁴ Σ ⁻		-2693.455888									

^aEnergies in parentheses are vertical energies calculated at $r = 2.055 \text{ \AA}$ for the four bound states discussed earlier.

^bWith respect to the centre of mass and with the direction AsCl; au = $ea_0 \approx 8.4784 \times 10^{-30} \text{ Cm}$.

^cExperimental data [33].

4.1.4 Results for BBr^+

As in the case of AsCl^+ , in the calculations using the MOLPRO program the density matrix averaged atomic natural orbital (ANO) spd basis sets of Pierloot et. al. [32] have been used for both atoms B and Br. For B 10s6p3d primitive Gaussian functions were contracted to 7s6p3d functions and for Br 17s15p9d functions were contracted to 9s9p5d. For both the boron and the bromine atoms single sets of f functions were added to this basis set with exponents $0.5 a_0^{-2}$ and $0.75 a_0^{-2}$, respectively resulting in 115 contracted Gaussian functions. For each spin and symmetry species molecular orbitals obtained from state averaged CASSCF calculations [146,147] were used in subsequent CI calculations. The active space is composed of the valence orbitals $9\sigma - 12\sigma$, 4π , 5π . As previously, for the CI calculations the internally contracted CI method of Knowles and Werner [150,151] has been used and the sets of reference configurations consisted of the configurations used in the CASSCF calculations.

Details of the numbers of roots considered (A), the sizes of the reference spaces (B), the numbers of contracted (C) and uncontracted (D) configurations are given in table 4.4. Here, due to the convergence problems in the CI calculations, we have considered more states than the numbers of roots defined from the combinations of $\text{Br}(^2\text{P}) + \text{B}^+(^1\text{S})$ and $\text{Br}^+(^3\text{P}) + \text{B}(^2\text{P})$ as presented in figure 4. These calculations have been carried out under C_{2v} symmetry and, where necessary, the wavefunctions have been examined and assigned to Σ or Δ .

Table 4.4 Details of configuration interaction calculations

State	A	B	C	D
$^2\Sigma^+$	6	616	526644	6498628
$^2\Pi$	5	588	453636	6327284
$^2\Sigma^-$	5	560	452379	6156011
$^4\Sigma^+$	5	320	429376	5484828
$^4\Pi$	4	336	357712	5444642
$^4\Sigma^-$	5	352	429408	5393652

The energy values obtained and the potential energy curves obtained for the $^2\Sigma^+$, $^2\Pi$, $^2\Sigma^-$, $^4\Sigma^-$, $^4\Sigma^+$ and $^4\Pi$ states, in turn, are represented in tables and figures 4.4.1 to 4.4.6, and the dominant configurations are given in tables 4.1.4.1.A to 4.1.4.6.A respectively. In the region of the equilibrium bond length ($r = 1.755 \text{ \AA}$) for the ground state the orbital 9σ is predominantly Br(4s), the orbital 10σ is an antibonding combination of B(2s), Br(4s) and Br(4p_σ), the orbital 11σ is a bonding combination of B(2s, 2p_σ) and Br(4p_σ), the orbital 12σ is an antibonding combination of B(2s,2p_σ) and Br(4s,4p_σ), the orbital 4π is predominantly Br(4p_π) and the orbital 5π is predominantly B(2p_π). As the dissociation asymptote is approached the orbitals 9σ , 11σ and 4π correlate with the orbitals 4s, 4p_σ and 4p_π on bromine whereas 10σ , 12σ and 5π correlate with 2s, 2p_σ and 2p_π on boron.

4.1.4.1 The CI calculations for the $^2\Sigma^+$ states of BBr⁺ with the ANO basis sets [32]

The energies, the potential curves and the dominant configurations are in table 4.4.1, figure 4.4.1 and table 4.1.4.1.A respectively.

Table 4.1.4.1.A Dominant configurations for the $^2\Sigma^+$ state

State	Configuration	Bond length
$1^2\Sigma^+$	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^4$	
$2^2\Sigma^+$	$\cdots 9\sigma^2 10\sigma^1 11\sigma^2 4\pi^4$	
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^3 5\pi^1$	
$^2\Delta$	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^3 5\pi^1$	

As shown in table 4.4.1 and figure 4.4.1, roots 1 and 3 are $^2\Sigma^+$ states and root 2 is a $^2\Delta$ state and they all are bound states. Root1 has quite a deep well and roots 2 and 3 have a reasonable amount of binding. Thus, spectroscopic constants have been calculated and the theoretical and experimental constants are compared in table 4.1.4.1.B.

Table 4.1.4.1.B Spectroscopic constants for the $^2\Sigma^+$ state

CONSTS	EXPT. ($1^2\Sigma^+$)	ROOT1($1^2\Sigma^+$)	ROOT2 ($2^2\Sigma^+$)	ROOT3($^2\Delta$)
ω_e/cm^{-1}	761.5 ^c	944.94	476.08	542.61
$\omega_e x_e/\text{cm}^{-1}$	6.3 ^c	5.6	0.017	3.14
B_0/cm^{-1}		0.56408	0.3667	0.4140
B_1/cm^{-1}		0.55988	0.3663	0.4089
B_2/cm^{-1}		0.55563	0.3658	0.4049
B_e/cm^{-1}		0.56620	0.3669	0.4161
α_e/cm^{-1}		0.0042	0.0004	0.0046
$R_e/\text{\AA}$		1.755	2.180	2.045

^cExperimental data [35].

However, for the $1^2\Sigma^+$ state there are errors of 24.1 % and 11.1 % between theory and experiment for the vibrational constant (ω_e), anharmonicity constant ($\omega_e x_e$) respectively. Therefore, our constants are in disagreement with experimental values.

4.1.4.2 The CI calculations for the $^2\Pi$ states of BBr^+ with the ANO basis sets [32]

The energies, the potential curves and the dominant configurations are, in turn, given in table 4.4.2 , figure 4.4.2 and table 4.1.4.2.A.

Table 4.1.4.2.A Dominant configurations for the $^2\Pi$ state

State	Configuration	Bond length
$1^2\Pi$	$\cdots 9\sigma^2 10\sigma^2 4\pi^4 5\pi^1$	$r \leq 1.7 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^2 4\pi^3$	$r \geq 1.8 \text{ \AA}$
$2^2\Pi$	$\cdots 9\sigma^2 10\sigma^2 11\sigma^2 4\pi^3$	$r \leq 1.7 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 4\pi^4 5\pi^1$	$1.8 \leq r \leq 2.8 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^2 4\pi^2 5\pi^1$	$r \geq 3.0 \text{ \AA}$
$3^2\Pi$	$\cdots 9\sigma^2 10\sigma^1 11\sigma^1 4\pi^4 5\pi^1$	$r \leq 1.6 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 4\pi^3 5\pi^2$	$1.7 \leq r \leq 2.0 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 12\sigma^1 4\pi^3$	$2.1 \leq r \leq 2.8 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^2 4\pi^2 5\pi^1$	$r \geq 3.0 \text{ \AA}$

From the figure 4.4.1, it can be seen that root1($1^2\Pi$) is weakly bound, root2($2^2\Pi$) has a local minimum and root3($3^2\Pi$) is repulsive. For roots 1 and 2 spectroscopic constants have been computed and presented in table 4.1.4.2.B together with experimental parameters [35] for the $2^2\Pi$ state.

Table 4.1.4.2.B Spectroscopic constants for the $^2\Pi$ state

CONSTS	ROOT1($1^2\Pi$)	EXPT. ($2^2\Pi$)	ROOT2($2^2\Pi$)
ω_e/cm^{-1}	335.37	813.8 ^c	791.76
$\omega_e x_e/\text{cm}^{-1}$	2.32	7.5 ^c	7.84
B_0/cm^{-1}	0.3612		0.5094
B_1/cm^{-1}	0.3134		0.5044
B_2/cm^{-1}	0.3101		0.4971
B_e/cm^{-1}	0.3178		0.5128
α_e/cm^{-1}	0.0030		0.0061
$R_e/\text{\AA}$	2.345		1.845

^cExperimental data from reference [35].

For ω_e , and $\omega_e x_e$ theoretical constants differ from experimental values [35] by 2.71 % and 4.53 %. Thus, there is reasonable agreement between theory and experiment for the $2^2\Pi$ state.

4.1.4.3 The CI calculations for the $^2\Sigma^-$ states of BBr^+ with the ANO basis sets [32]

The energies, the potential curves and the dominant configurations are given in table 4.4.3, figure 4.4.3 and table 4.1.4.3.A respectively. Roots 1 and 3 are $^2\Sigma^-$ states and root2 is a $^2\Delta$ state.

Table 4.1.4.3.A Dominant configurations for the $^2\Sigma^-$ state

State	Configuration	Bond length
$1^2\Sigma^-$	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^3 5\pi^1$	
$2^2\Sigma^-$	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^3 5\pi^1$	$r \leq 2.8 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^2 12\sigma^1 4\pi^2$	$r \geq 2.9 \text{ \AA}$

Roots 1 and 2 are reasonably bound whereas root3 is repulsive. Spectroscopic constants have been calculated for the $1^2\Sigma^-$ and $^2\Delta$ states. For the $^2\Delta$ state the calculated constants and the dominant configurations have already been reported in subsection 4.1.4.1. Thus, here only the calculated values for the $1^2\Sigma^-$ state are given in table 4.1.4.3.B. No experimental data are available for these states.

Table 4.1.4.3.B Spectroscopic constants of the $^2\Sigma^-$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$1^2\Sigma^-$	547.83	4.27	0.4133	0.4090	0.4047	0.4155	0.0043	2.05

4.1.4.4 The CI calculations for the $^4\Sigma^-$ states of BBr^+ with the ANO basis sets [32]

The energies, potential energy curves and the dominant configurations are given in table 4.4.4, figure 4.4.4 and table 4.1.4.4.A respectively. Roots 2 and 3 are $^4\Sigma^-$ states and root1 is a $^4\Delta$ state.

Table 4.1.4.4.A Dominant configurations for the $^4\Sigma^-$ states

State	Configuration	Bond length
$1^4\Sigma^-$	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^3 5\pi^1$	
$2^4\Sigma^-$	$\cdots 9\sigma^2 10\sigma^1 4\pi^4 5\pi^2$	$r \leq 1.9 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^2 12\sigma^1 4\pi^2$	$r \geq 2.0 \text{ \AA}$
$^4\Delta$	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^3 5\pi^1$	

As shown in figure 4.4.4, roots 1 and 2 are bound states and root 3 is repulsive. Thus, for the $^4\Delta$ and $1^4\Sigma^-$ states spectroscopic constants have been calculated and are given in table 4.1.4.4.B. However, for these states no experimental spectroscopic data have been reported.

Table 4.1.4.4.B Spectroscopic constants of the $1^4\Sigma^-$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$1^4\Sigma^-$	512.86	3.29	0.4073	0.4029	0.3983	0.4096	0.0044	2.065
$^4\Delta$	554.23	4.09	0.4220	0.4176	0.4132	0.4242	0.0044	2.030

4.1.4.5 The CI calculations for the $^4\Sigma^+$ state of BBr^+ with the ANO basis sets [32]

Table 4.4.5, figure 4.4.5 and table 4.1.4.5.A give the energies, the potential curves and the dominant configurations respectively. Root1 and root2 are $^4\Sigma^+$ and $^4\Delta$ states respectively.

Table 4.1.4.5.A Dominant configurations for the $^4\Sigma^+$ state

State	Configuration	Bond length
$^4\Sigma^+$	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^3 5\pi^1$	

Both states are well bound. For the $^4\Delta$ state the calculated constants and the dominant configurations were given in the previous section. The calculated spectroscopic

constants for the $^4\Sigma^+$ state are given in table 4.1.4.5.B. but for the $^4\Sigma^+$ state there are no experimental data.

Table 4.1.4.5.B Spectroscopic constants of the $^4\Sigma^+$ state

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$^4\Sigma^+$	597.97	4.30	0.4409	0.4364	0.4319	0.4431	0.0045	1.985

4.1.4.6 The CI calculations for the $^4\Pi$ states of BBr^+ with the ANO basis sets [32]

The energies, the potential curves and the dominant configurations are presented in table 4.4.6, figure 4.4.6 and table 4.1.4.6.A respectively.

Table 4.1.4.6.A Dominant configurations for the $^4\Pi$ state

State	Configuration	Bond length
$1^4\Pi$	$\cdots 9\sigma^2 10\sigma^1 11\sigma^1 4\pi^4 5\pi^1$	$r \leq 2.1 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 12\sigma^1 4\pi^3$	$r \geq 2.2 \text{ \AA}$
$2^4\Pi$	$\cdots 9\sigma^2 10\sigma^2 4\pi^3 5\pi^2$	$r \leq 1.8 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^1 12\sigma^1 4\pi^3$	$1.9 \leq r \leq 2.1 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^1 11\sigma^1 4\pi^4 5\pi^1$	$2.2 \leq r \leq 2.3 \text{ \AA}$
	$\cdots 9\sigma^2 10\sigma^2 11\sigma^2 4\pi^2 5\pi^1$	$r \geq 2.4 \text{ \AA}$

From the figure 4.4.6, it can be seen that both states are repulsive so theoretical constants have not been calculated.

4.1.4.7 General discussion for BBr^+

Figures 4.4.9 and 4.4.10 show the potential energy curves for the doublet and quartet states respectively. Compared to the other three molecular ions considered NF^+ , PCl^+ and AsCl^+ , there are many more bound states, namely $1^2\Sigma^+$, $2^2\Sigma^+$, $^2\Delta$, $1^2\Pi$, $2^2\Pi$, $2^2\Sigma^-$, $1^4\Sigma^-$, $^4\Delta$ and $^4\Sigma^+$. The $1^2\Sigma^+$ state is the ground state, $X^2\Sigma^+$, with an equilibrium bond

length of $r = 1.755 \text{ \AA}$. The $1^2\Sigma^+$ and $2^2\Delta$ states lie very close. For clarity we have not included the $1^2\Sigma^+$ state in figure 4.4.9. The difference in energy between the two $2^2\Sigma^+$ state curves at $r = 4.0 \text{ \AA}$ is 3.2 eV, which is in reasonable agreement with the experimental energy difference of 3.54 eV for the two dissociation asymptotes. Unlike AlF^+ , AlCl^+ [44], GaF^+ , GaCl^+ [45], as the internuclear distance is varied the $X^2\Sigma^+$ state is represented well by a single dominant configuration. For the group IIIa monohalide cations mentioned above [44,45] the lowest $2^2\Pi$ states are repulsive whereas for BBr^+ the lowest $2^2\Pi$ state has a shallow minimum at an equilibrium bond length of $r = 2.35 \text{ \AA}$. Inspection of the dominant configurations in table 4.1.4.2.A for the $2^2\Pi$ state shows that there is an avoided intersection between the $1^2\Pi$ and $2^2\Pi$ states in the region of 1.75 \AA , and the $3^2\Pi$ state, which is repulsive, has several avoided crossings with higher states at 1.6, 2.0 and 2.9 \AA . For the $X^2\Sigma^+$, $2^2\Sigma^+$, $1^2\Pi$, $2^2\Pi$ and $2^2\Delta$ states the dipole moments and the dipole moment functions are presented in table 4.4.7 and figure 4.4.7. The dipole moments have been reported with the centre of mass chosen as origin and in the direction BBr . As the internuclear distance is increased the $X^2\Sigma^+$ state dissociates to $\text{B}^+ + \text{Br}$, and the dipole moment becomes increasingly negative and is seen to approach a linear function of r . For the $1^2\Pi$ state there is a rapid change at $r = 1.75 \text{ \AA}$ where there is an avoided intersection with the $2^2\Pi$ state. For the $2^2\Pi$ state there are rapid changes at $r = 1.75 \text{ \AA}$, and at $r = 2.8 \text{ \AA}$ where there is an avoided crossing with the $3^2\Pi$ state. As the bond length becomes longer, the distance of the Br^+ fragment from the centre of mass increases and the

dipole moment functions for the $2^2\Sigma^+$, $2^2\Pi$ and $2^2\Delta$ states become increasingly positive. Table 4.1.4.7.A includes the energies of all of the bound states at their equilibrium bond lengths, the vertical energies of all states at the equilibrium bond length of $r = 1.755$ Å for the $X^2\Sigma^+$ state, the theoretical spectroscopic constants, T_e values and dipole moments. Yamaguchi *et al.* [35] have assigned their spectra to the $A^2\Pi_r \rightarrow X^2\Sigma^+$ transition. Considering the theoretical potential energy curves this system would be expected to be the $2^2\Pi_r \rightarrow X^2\Sigma^+$ transition. However, for these two states there is poor agreement between the calculated spectroscopic constants and the experimental values of $\omega'_e = 813.8$ cm⁻¹, $\omega''_e = 761.5$ cm⁻¹ and $T_e = 20171$ cm⁻¹ (2.5 eV) observed by Yamaguchi *et al.* [35]. To make sure that our calculated potential energy curves were of reasonable accuracy we have carried out calculations for the $1^1\Sigma^+$ state at neutral BBr for which spectroscopic constants have been obtained from Destoky *et al.* [160] in a rotational analysis of ten bands in the $A^1\Pi \rightarrow X^1\Sigma^+$ transition detected in emission. We have used the same basis set as in the calculations for BBr⁺. Molecular orbitals were generated from a CASSCF calculation which has the same active space as for BBr⁺, and the configurations included in the CASSCF calculation were used as reference configurations for a CI calculation of the $X^1\Sigma^+$ state. Table 4.4.9 and figure 4.4.11 give the theoretical energy values and the calculated potential energy curve for the $X^1\Sigma^+$ state of BBr. As shown in figure 4.4.11, the potential curve is bound, and spectroscopic constants have been calculated and are given in table 4.1.4.7.B.

Table 4.1.4.7.B Spectroscopic constants of the $^1\Sigma^+$ state for BBr

Consts	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$R_e/\text{\AA}$
$^1\Sigma^+$	697.26	3.94	0.48570	0.48147	0.47729	0.48779	0.00421	1.897
Expt.	687.03	4.86				0.48918	0.00356	

For ω_e and B_e , it is seen that our values differ from the experimental data by 1.49 % and 0.28 % and thus, our constants agree well with the experimental values. Therefore, we are confident that our calculations for BBr $^+$ should produce reasonable data for the spectroscopic constants. It is very difficult to explain the observations of Yamaguchi *et al.* [35]. Even though our value of ω_e for the $2^2\Pi$ state is in reasonable agreement with their value of ω'_e , the $2^2\Pi$ state is computed to lie 4.59 eV higher than the $X^2\Sigma^+$ state and a transition between these states would result in emission in the region of 270 nm. Glenewinkel-Meyer *et al.* [36] believed this transition to lie at 300 nm or less. Calculated vertical transition energies from the $2^2\Pi$ to the $1^2\Sigma^-$ state and $^2\Delta$ states are 0.78 eV and such transition energies would be expected not to be comparable with the T_e value of 2.5 eV obtained by Yamaguchi *et al.* [35]. Since there is a significant difference between the equilibrium bond lengths for the $X^2\Sigma^+$ and $2^2\Sigma^+$ states, a broad emission spectrum would be expected for this transition. Vertical transition energies at $r = 1.755 \text{ \AA}$ and 2.180 \AA are 5.9 eV and 3.5 eV respectively. Thus, it would be expected that the emission will occur in the wavelength range 210 - 350 nm. The electronic transition moments and the electronic transition moment functions for the $2^2\Sigma^+ \rightarrow X^2\Sigma^+$ and $2^2\Pi \rightarrow X^2\Sigma^+$ transitions are given in table 4.4.8 and figure 4.4.8 respectively. Figure 4.4.8 shows that the

electronic transition dipole moment for the $2^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition ranges from 0.30 au. to 0.22 au. for the bond lengths from 1.8 Å and 2.2 Å. This is significantly smaller than the values reported by Glenewinkel-Meyer *et al.* [44] for AlF^+ and AlCl^+ . Thus, for BBr^+ it would be expected that this transition would be less intense. In the vicinity of $r = 1.8$ Å the electronic transition dipole moment for the $2^2\Pi \rightarrow X^2\Sigma^+$ transition is somewhat larger. The avoided crossing between the 1 and $2^2\Pi$ state occurs in the region of $r = 1.755$ Å which is close to the equilibrium bond length for the $2^2\Pi$ state, and the population of this state may be decreased by predissociation to the $1^2\Pi$ state.

For the quartet states, only the $^4\Sigma^+$, $1^4\Sigma^-$ and $^4\Delta$ states, resulting from the configuration $\cdots 9\sigma^2 10\sigma^2 11\sigma^1 4\pi^3 5\pi^1$, are reasonably bound. These close-lying states are described well by one dominant configuration, and have comparable spectroscopic constants. Due to the closeness of the calculated potential energy curves these quartet states would seem to be unimportant for optical spectroscopy. We have carried out a comprehensive investigation of the low-lying electronic states for BBr^+ and are confident that our calculated spectroscopic constants should be reasonable predictions for experimental data. The disagreement with the data of Yamaguchi *et al.* [45] suggests that the spectroscopy of this species should be reinvestigated.

4.4.1 The CI results for the $^2\Sigma^+$ states of BBr^+ with the ANO basis sets [32]

Table 4.4.1 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5	ROOT6
1.4	-2596.848948	-2596.539399	-2596.542443	-2596.491478	-2596.487893	-2596.407976
1.5	-2596.929338	-2596.651809	-2596.648279	-2596.593122	-2596.590405	-2596.523860
1.6	-2596.970862	-2596.722760	-2596.714660	-2596.657884	-2596.653746	-2596.601043
1.7	-2596.987422	-2596.766128	-2596.755668	-2596.696176	-2596.693577	-2596.652706
1.8	-2596.988335	-2596.791169	-2596.780748	-2596.717379	-2596.717530	-2596.687440
1.9	-2596.979903	-2596.804108	-2596.795919	-2596.727869	-2596.731056	-2596.710489
2.0	-2596.966447	-2596.809166	-2596.804735	-2596.739095	-2596.732054	-2596.724245
2.1	-2596.950953	-2596.809198	-2596.809124	-2596.745795	-2596.732979	-2596.729699
2.2	-2596.935483	-2596.806114	-2596.810084	-2596.751236	-2596.732672	-2596.730373
2.3	-2596.921414	-2596.801180	-2596.808164	-2596.754543	-2596.732323	-2596.729614
2.4	-2596.909534	-2596.795236	-2596.803803	-2596.755833	-2596.732436	-2596.728905
2.5	-2596.900087	-2596.788848	-2596.797552	-2596.755545	-2596.733020	-2596.728722
2.6	-2596.892884	-2596.782411	-2596.790112	-2596.754151	-2596.733829	-2596.729004
2.7	-2596.887499	-2596.776232	-2596.782221	-2596.752062	-2596.734559	-2596.729441
2.8	-2596.883495	-2596.770554	-2596.774549	-2596.749601	-2596.734949	-2596.729679
2.9	-2596.880488	-2596.765570	-2596.767637	-2596.746920	-2596.734793	-2596.729429
3.0	-2596.878204	-2596.761438	-2596.761949	-2596.743973	-2596.733961	-2596.728558
3.1	-2596.876445	-2596.758222	-2596.757783	-2596.740584	-2596.732414	-2596.727117
3.2	-2596.875073	-2596.755856	-2596.755066	-2596.736751	-2596.730257	-2596.725275
3.5	-2596.872342	-2596.752070	-2596.751603	-2596.725159	-2596.722151	-2596.719079
4.0	-2596.867066	-2596.751109	-2596.751089	-2596.711585	-2596.706013	-2596.705913
4.5	-2596.864209	-2596.748079	-2596.748157	-2596.705294	-2596.699505	-2596.699030
5.0	-2596.860571	-2596.743520	-2596.743589	-2596.698520	-2596.693708	-2596.693706

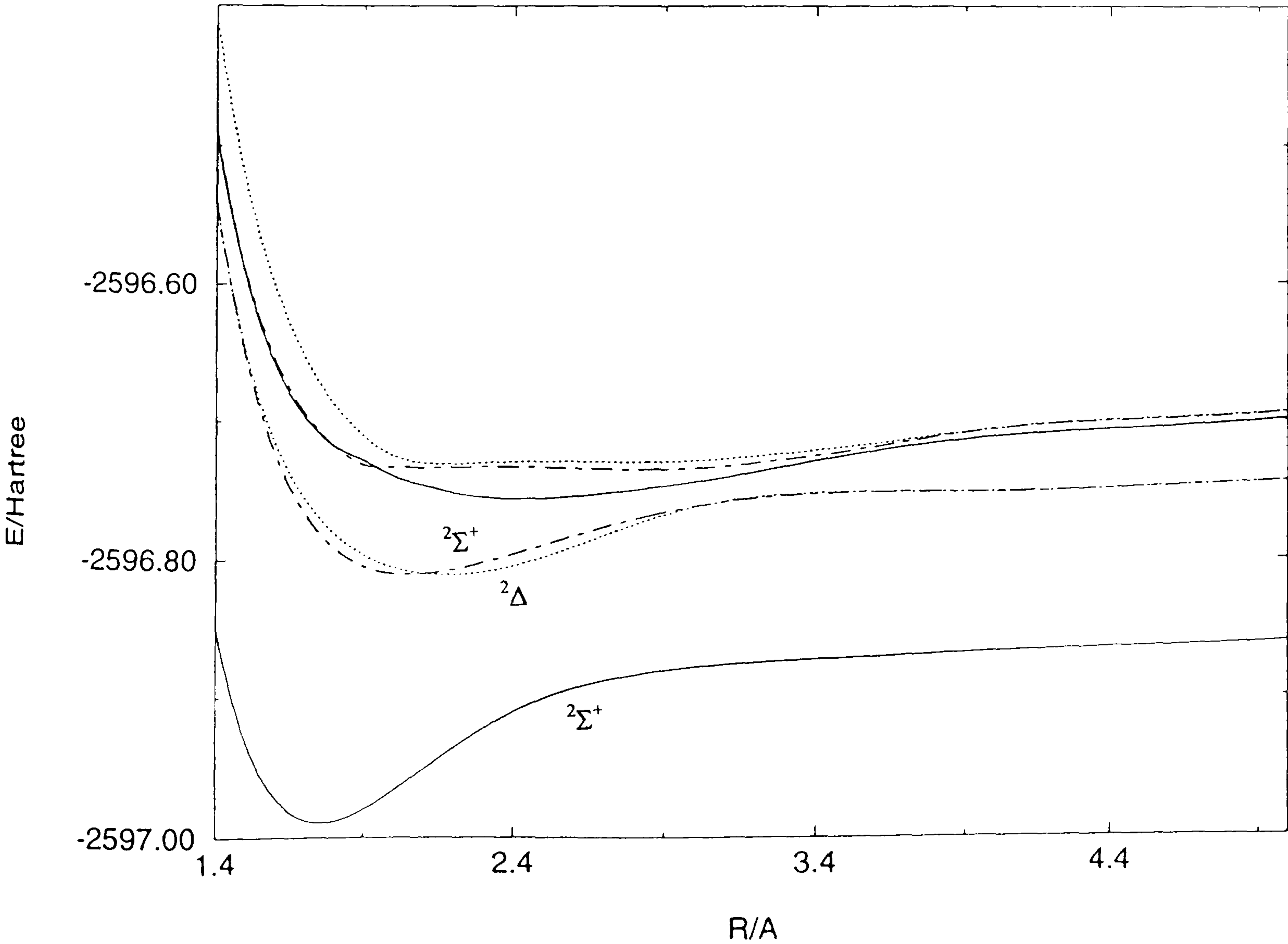
$^2\Sigma^+$

$^2\Delta$

$^2\Sigma^+$

E/Hartree

Figure 4.4.1 Calculated potential energy curves



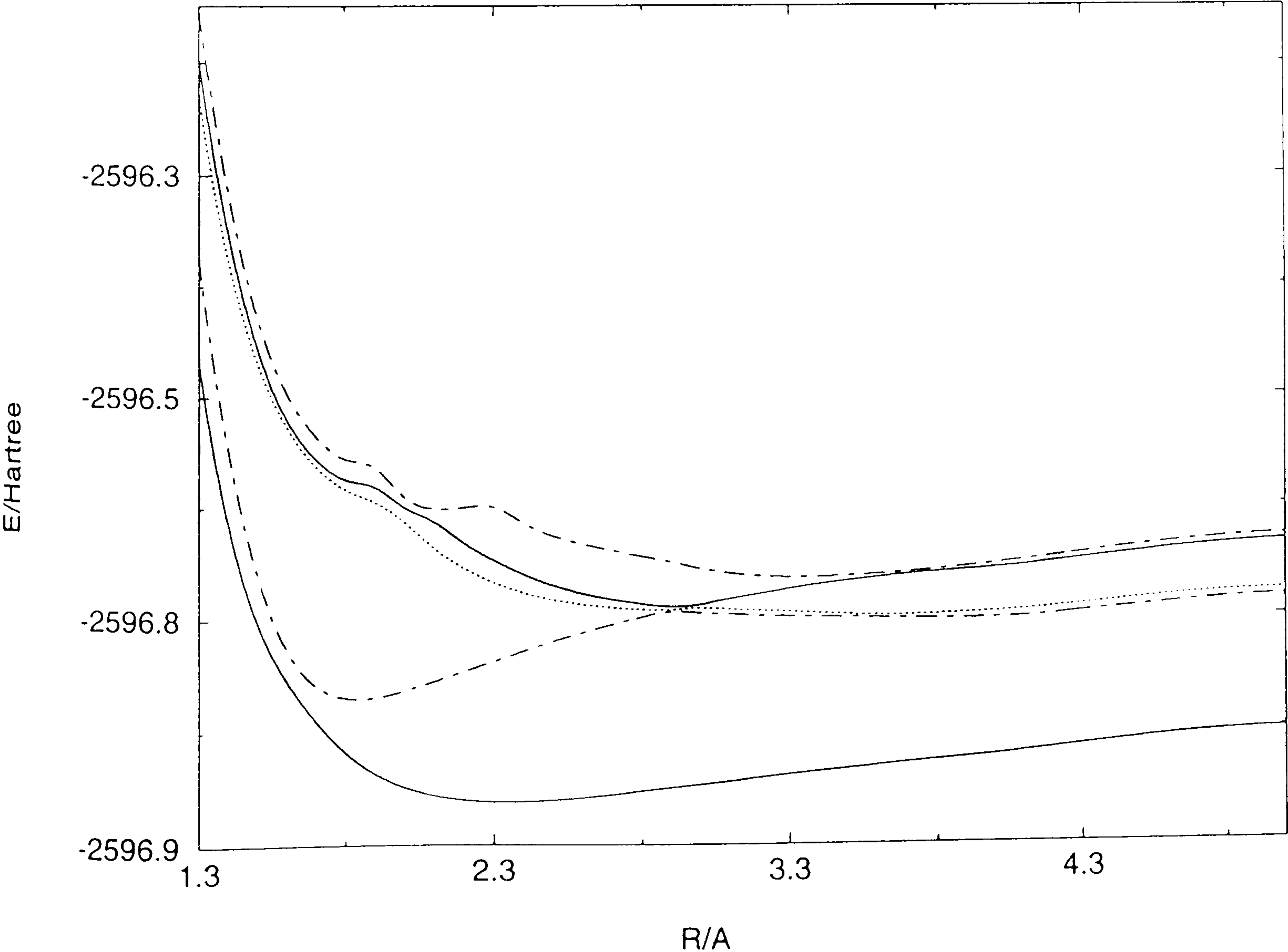
4.4.2 The CI results for the $^2\Pi$ states of BBr^+ with the ANO basis sets [32]

Table 4.4.2 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.3	-2596.517074	-2596.424142	-2596.276667	-2596.246088	-2596.204170
1.4	-2596.662854	-2596.595790	-2596.424334	-2596.400018	-2596.363678
1.5	-2596.750961	-2596.706871	-2596.516918	-2596.503499	-2596.476096
1.6	-2596.803430	-2596.775128	-2596.575471	-2596.568383	-2596.544809
1.7	-2596.840421	-2596.808774	-2596.611686	-2596.605160	-2596.584615
1.8	-2596.868096	-2596.819799	-2596.632833	-2596.623788	-2596.605159
1.9	-2596.886839	-2596.819744	-2596.644283	-2596.630761	-2596.613089
2.0	-2596.898884	-2596.813589	-2596.661821	-2596.648791	-2596.639610
2.1	-2596.906252	-2596.805515	-2596.685337	-2596.661892	-2596.650184
2.2	-2596.910261	-2596.796509	-2596.703298	-2596.680984	-2596.649364
2.3	-2596.911880	-2596.787365	-2596.716546	-2596.696620	-2596.649061
2.4	-2596.911816	-2596.778242	-2596.726071	-2596.709507	-2596.663704
2.5	-2596.910515	-2596.769680	-2596.732626	-2596.719574	-2596.675565
2.6	-2596.908394	-2596.762015	-2596.736989	-2596.727190	-2596.683080
2.7	-2596.905756	-2596.754991	-2596.739880	-2596.732895	-2596.689092
2.8	-2596.902851	-2596.748639	-2596.741965	-2596.736881	-2596.694294
2.9	-2596.899951	-2596.744386	-2596.742432	-2596.739285	-2596.699756
3.0	-2596.897153	-2596.745481	-2596.740942	-2596.737528	-2596.705501
3.1	-2596.894250	-2596.746757	-2596.742204	-2596.732789	-2596.709934
3.2	-2596.891412	-2596.747882	-2596.743598	-2596.728405	-2596.712732
3.5	-2596.883694	-2596.750384	-2596.747666	-2596.717441	-2596.713305
4.0	-2596.872408	-2596.751091	-2596.745631	-2596.706246	-2596.702392
4.5	-2596.859397	-2596.741442	-2596.734925	-2596.692774	-2596.687348
5.0	-2596.851102	-2596.733347	-2596.727465	-2596.683131	-2596.678398

E/Hartree

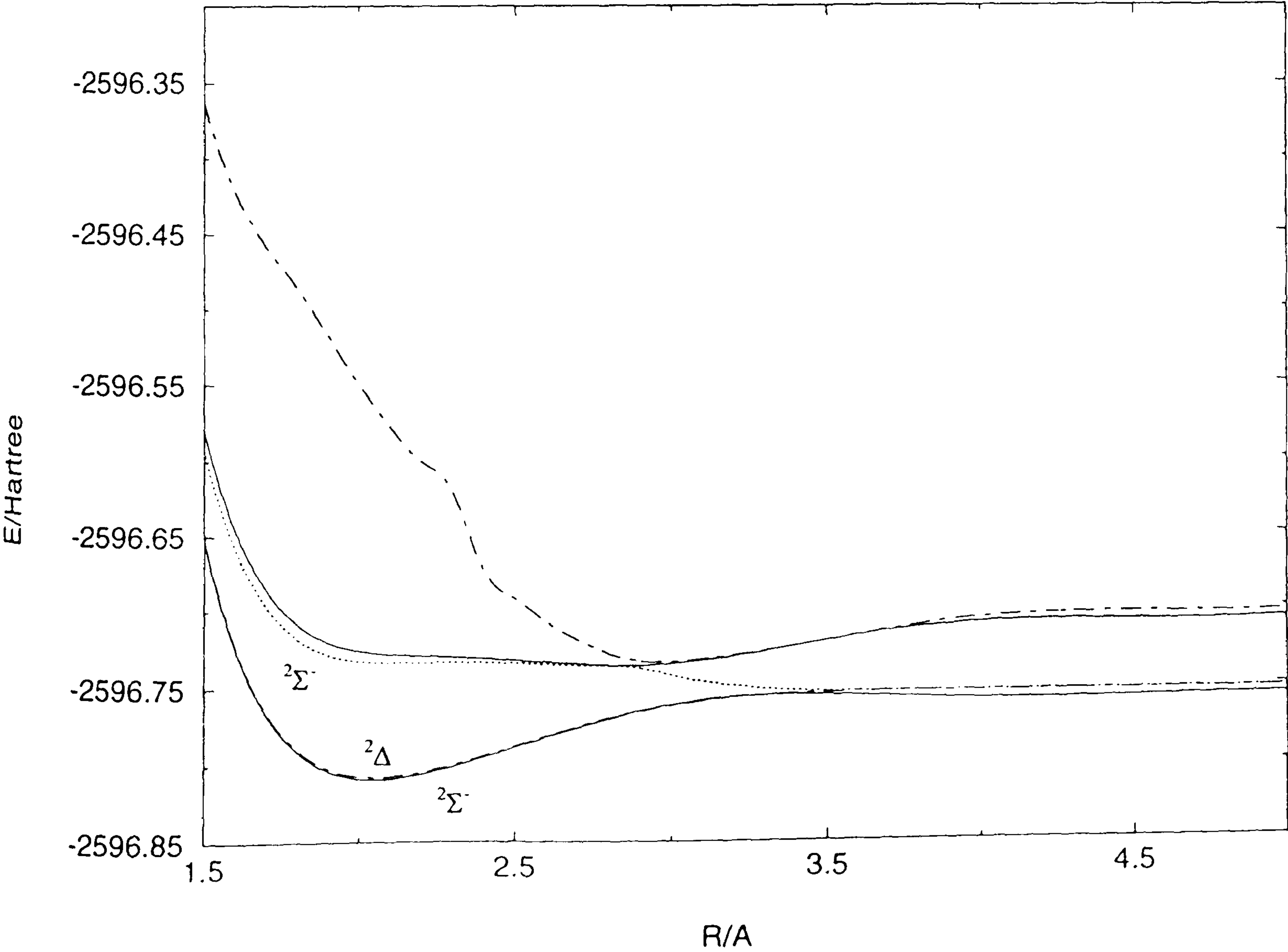
Figure 4.4.2 Calculated potential energy curves



4.4.3 The CI results for the $^2\Sigma^-$ states of BBr^+ with the ANO basis sets [32]

Table 4.4.3 Theoretical energy values					
R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-2596.651952	-2596.650550	-2596.592320	-2596.578642	-2596.362793
1.6	-2596.722973	-2596.721475	-2596.657106	-2596.644772	-2596.421067
1.7	-2596.766350	-2596.764784	-2596.695544	-2596.684616	-2596.457524
1.8	-2596.791064	-2596.789453	-2596.717207	-2596.707658	-2596.484876
1.9	-2596.803983	-2596.802362	-2596.727732	-2596.719577	-2596.516797
2.0	-2596.809051	-2596.807459	-2596.732036	-2596.725192	-2596.549103
2.1	-2596.809103	-2596.807568	-2596.733094	-2596.727452	-2596.577013
2.2	-2596.806047	-2596.804592	-2596.732924	-2596.728355	-2596.600163
2.3	-2596.801139	-2596.799779	-2596.732717	-2596.729078	-2596.619845
2.4	-2596.794885	-2596.793697	-2596.732827	-2596.730073	-2596.672096
2.5	-2596.788501	-2596.787423	-2596.733534	-2596.731426	-2596.691351
2.6	-2596.782085	-2596.781114	-2596.734447	-2596.732875	-2596.706612
2.7	-2596.775945	-2596.775076	-2596.735239	-2596.734161	-2596.718560
2.8	-2596.770356	-2596.769583	-2596.735625	-2596.735221	-2596.727627
2.9	-2596.764852	-2596.765533	-2596.737378	-2596.735377	-2596.732794
3.0	-2596.761060	-2596.761646	-2596.741939	-2596.734348	-2596.733048
3.1	-2596.758266	-2596.758744	-2596.746015	-2596.732514	-2596.731599
3.2	-2596.756389	-2596.756720	-2596.749155	-2596.730008	-2596.729305
3.5	-2596.755632	-2596.753917	-2596.752987	-2596.720273	-2596.719949
4.0	-2596.758519	-2596.753148	-2596.752832	-2596.709082	-2596.706106
4.5	-2596.757873	-2596.752703	-2596.752538	-2596.708141	-2596.703044
5.0	-2596.756708	-2596.752623	-2596.752134	-2596.706910	-2596.702921
	$^2\Sigma^-$	$^2\Delta$	$^2\Sigma^-$		
E/Hartree					

Figure 4.4.3 Calculated potential energy curves



4.4.4 The CI results for the $^4\Sigma^-$ states of BBr^+ with the ANO basis sets [32]

Table 4.4.4 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-2596.674880	-2596.656706	-2596.415021	-2596.350633	-2596.308401
1.6	-2596.742524	-2596.726845	-2596.473460	-2596.429447	-2596.388374
1.7	-2596.783120	-2596.769839	-2596.510096	-2596.479760	-2596.441423
1.8	-2596.805950	-2596.794865	-2596.533772	-2596.512628	-2596.483685
1.9	-2596.817131	-2596.808044	-2596.552179	-2596.541667	-2596.527677
2.0	-2596.820809	-2596.813393	-2596.577612	-2596.574847	-2596.560031
2.1	-2596.820053	-2596.813970	-2596.608737	-2596.603318	-2596.592723
2.2	-2596.816542	-2596.811594	-2596.637553	-2596.626438	-2596.618774
2.3	-2596.811441	-2596.807423	-2596.662598	-2596.645103	-2596.639242
2.4	-2596.805533	-2596.802272	-2596.683494	-2596.660041	-2596.655392
2.5	-2596.799331	-2596.796681	-2596.700497	-2596.671885	-2596.668130
2.6	-2596.793179	-2596.791018	-2596.714108	-2596.681192	-2596.678128
2.7	-2596.787288	-2596.785521	-2596.724860	-2596.688420	-2596.685904
2.8	-2596.781796	-2596.780345	-2596.733257	-2596.693951	-2596.691879
2.9	-2596.776783	-2596.775587	-2596.739737	-2596.698098	-2596.696385
3.0	-2596.772287	-2596.771303	-2596.744678	-2596.701119	-2596.699699
3.1	-2596.768335	-2596.767527	-2596.748390	-2596.703244	-2596.702062
3.2	-2596.764906	-2596.764251	-2596.751129	-2596.704613	-2596.703613
3.5	-2596.757397	-2596.757409	-2596.755060	-2596.705884	-2596.705277
4.0	-2596.748957	-2596.754249	-2596.748639	-2596.702112	-2596.701840

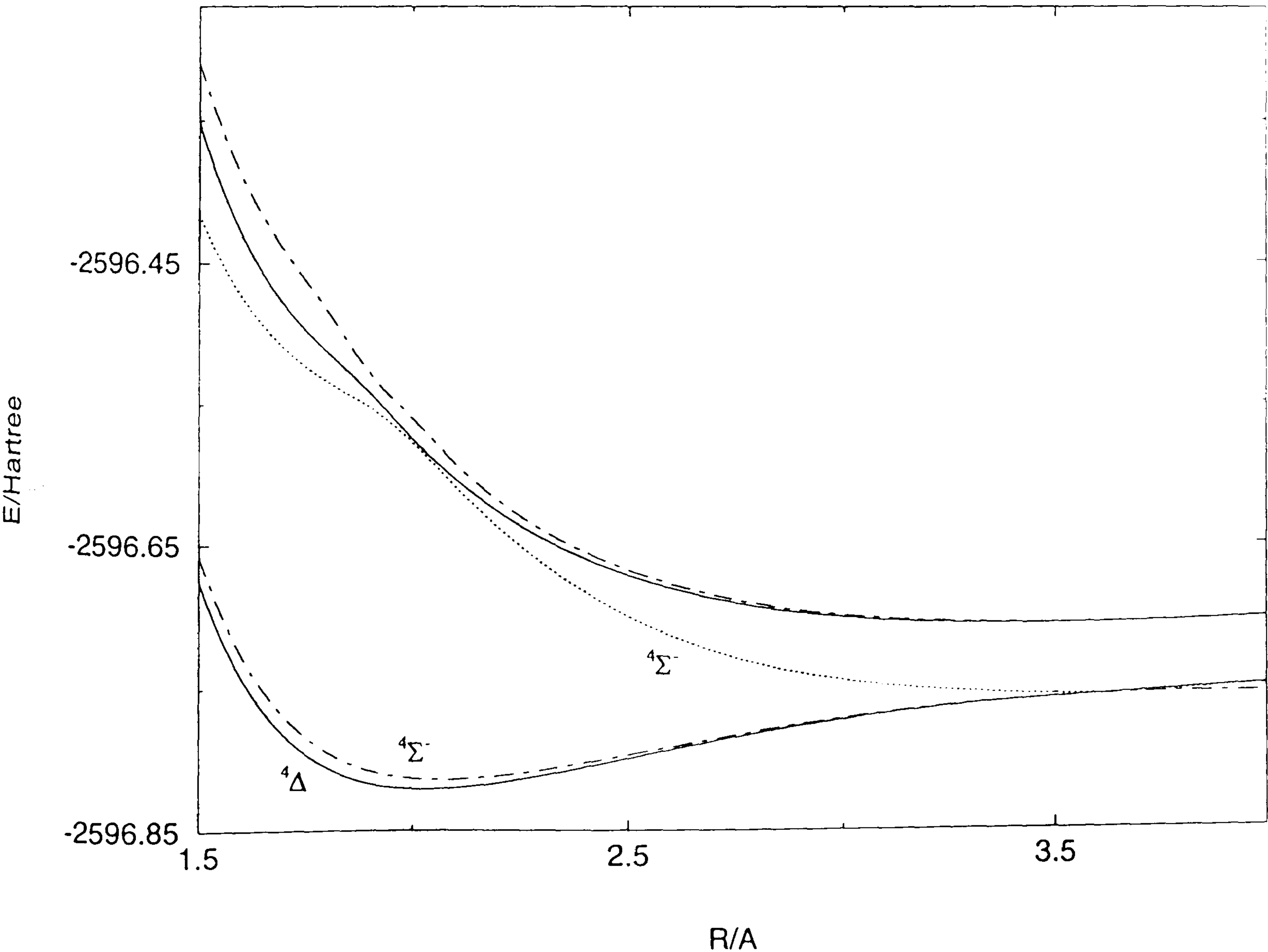
$^4\Delta$

$^4\Sigma^-$

$^4\Sigma^-$

E/Hartree

Figure 4.4.4 Calculated potential energy curves



4.4.5 The CI results for the $^4\Sigma^+$ states of BBr^+ with the ANO basis sets [32]

Table 4.4.5 Theoretical energy values

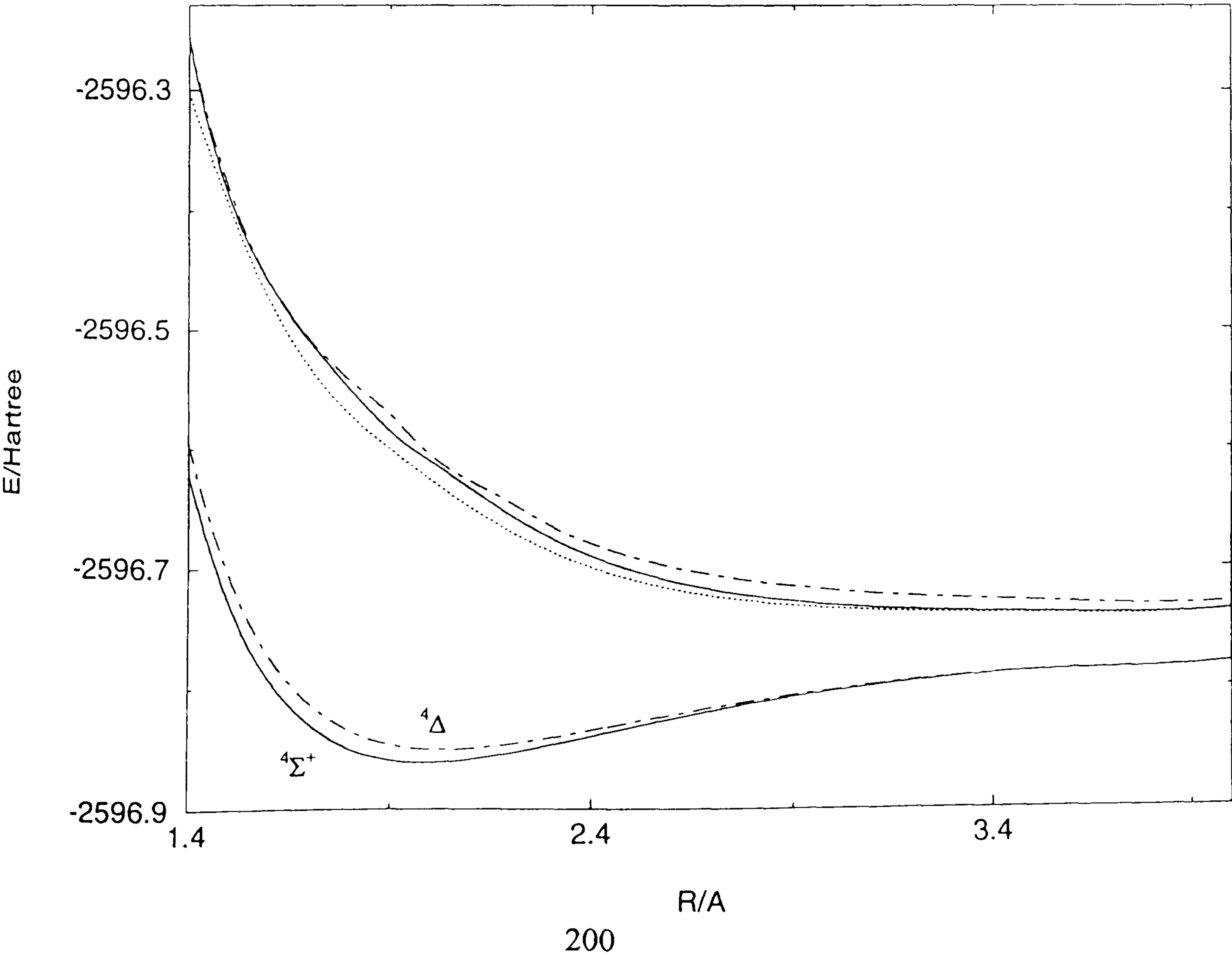
R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.4	-2596.590907	-2596.565362	-2596.271836	-2596.227559	-2596.227047
1.5	-2596.697125	-2596.674209	-2596.364884	-2596.356447	-2596.349990
1.6	-2596.762194	-2596.741991	-2596.443364	-2596.428978	-2596.428172
1.7	-2596.800214	-2596.782665	-2596.501972	-2596.479565	-2596.477630
1.8	-2596.820552	-2596.805501	-2596.541822	-2596.520168	-2596.512814
1.9	-2596.829559	-2596.816806	-2596.570305	-2596.555800	-2596.541992
2.0	-2596.831414	-2596.820711	-2596.595694	-2596.580523	-2596.575508
2.1	-2596.828876	-2596.819954	-2596.619700	-2596.603753	-2596.597419
2.2	-2596.823740	-2596.816338	-2596.640017	-2596.626777	-2596.616185
2.3	-2596.817202	-2596.811091	-2596.656410	-2596.645274	-2596.635655
2.4	-2596.810155	-2596.805145	-2596.669395	-2596.660096	-2596.649733
2.5	-2596.803033	-2596.798945	-2596.679587	-2596.671860	-2596.660661
2.6	-2596.796124	-2596.792800	-2596.687496	-2596.681100	-2596.669262
2.7	-2596.789614	-2596.786917	-2596.693566	-2596.688299	-2596.676057
2.8	-2596.783599	-2596.781416	-2596.698159	-2596.693843	-2596.681436
2.9	-2596.778134	-2596.776365	-2596.701581	-2596.698059	-2596.685700
3.0	-2596.773236	-2596.771798	-2596.704076	-2596.701212	-2596.689085
3.1	-2596.768895	-2596.767725	-2596.705838	-2596.703519	-2596.691775
3.2	-2596.765091	-2596.764126	-2596.707014	-2596.705124	-2596.693902
3.5	-2596.756657	-2596.756102	-2596.708262	-2596.707266	-2596.697813
4.0	-2596.749654	-2596.749391	-2596.706545	-2596.706159	-2596.699803

$^4\Sigma^+$

$^4\Delta$

E/Hartree

Figure 4.4.5 Calculated potential energy curves

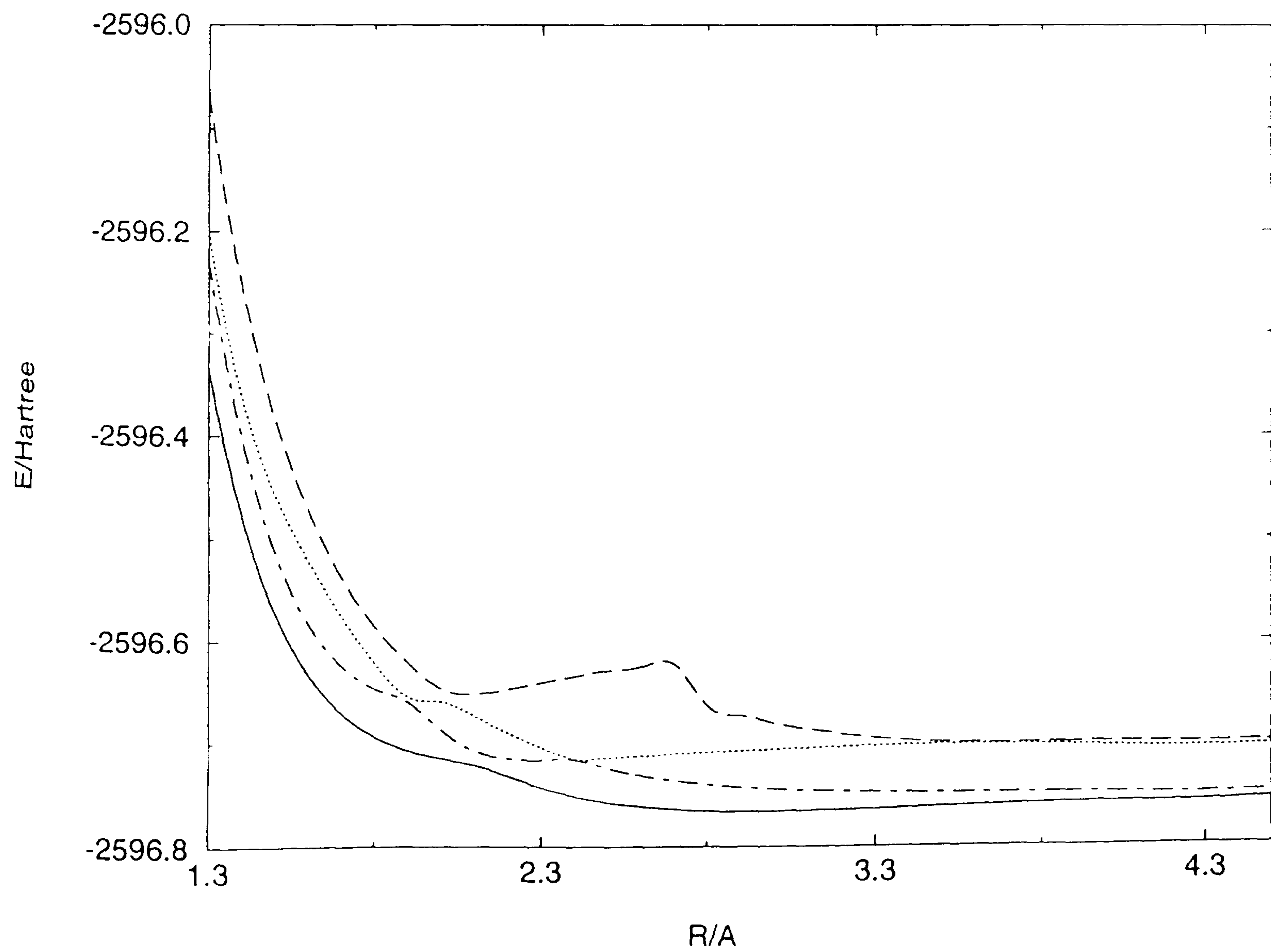


4.4.6 The CI results for the $^4\Pi$ states of BBr^+ with the ANO basis sets [32]

Table 4.4.6 Theoretical energy values				
R/Å	ROOT1	ROOT2	ROOT3	ROOT4
1.3	-2596.331302	-2596.227449	-2596.198799	-2596.065048
1.4	-2596.479753	-2596.403027	-2596.362708	-2596.255158
1.5	-2596.574313	-2596.515238	-2596.458515	-2596.384628
1.6	-2596.634193	-2596.584233	-2596.522400	-2596.473768
1.7	-2596.671051	-2596.624543	-2596.576196	-2596.537791
1.8	-2596.693225	-2596.646279	-2596.621279	-2596.585071
1.9	-2596.706303	-2596.659575	-2596.654294	-2596.620643
2.0	-2596.714108	-2596.686857	-2596.659344	-2596.646340
2.1	-2596.720502	-2596.706591	-2596.673152	-2596.651628
2.2	-2596.731311	-2596.714239	-2596.689951	-2596.646986
2.3	-2596.742589	-2596.715509	-2596.703788	-2596.640873
2.4	-2596.751160	-2596.715400	-2596.714461	-2596.634809
2.5	-2596.757158	-2596.723736	-2596.713585	-2596.629541
2.6	-2596.761125	-2596.730630	-2596.711841	-2596.625424
2.7	-2596.763633	-2596.735984	-2596.709901	-2596.623617
2.8	-2596.765479	-2596.739494	-2596.708547	-2596.664323
2.9	-2596.765934	-2596.742311	-2596.707124	-2596.673707
3.0	-2596.765817	-2596.744374	-2596.705805	-2596.681178
3.1	-2596.765330	-2596.745866	-2596.704615	-2596.687027
3.2	-2596.764625	-2596.746929	-2596.703574	-2596.691550
3.5	-2596.762046	-2596.748493	-2596.701551	-2596.699291
4.0	-2596.758062	-2596.748758	-2596.703281	-2596.699543
4.5	-2596.754866	-2596.748190	-2596.702851	-2596.699049

E/Hartree

Figure 4.4.6 Calculated potential energy curves



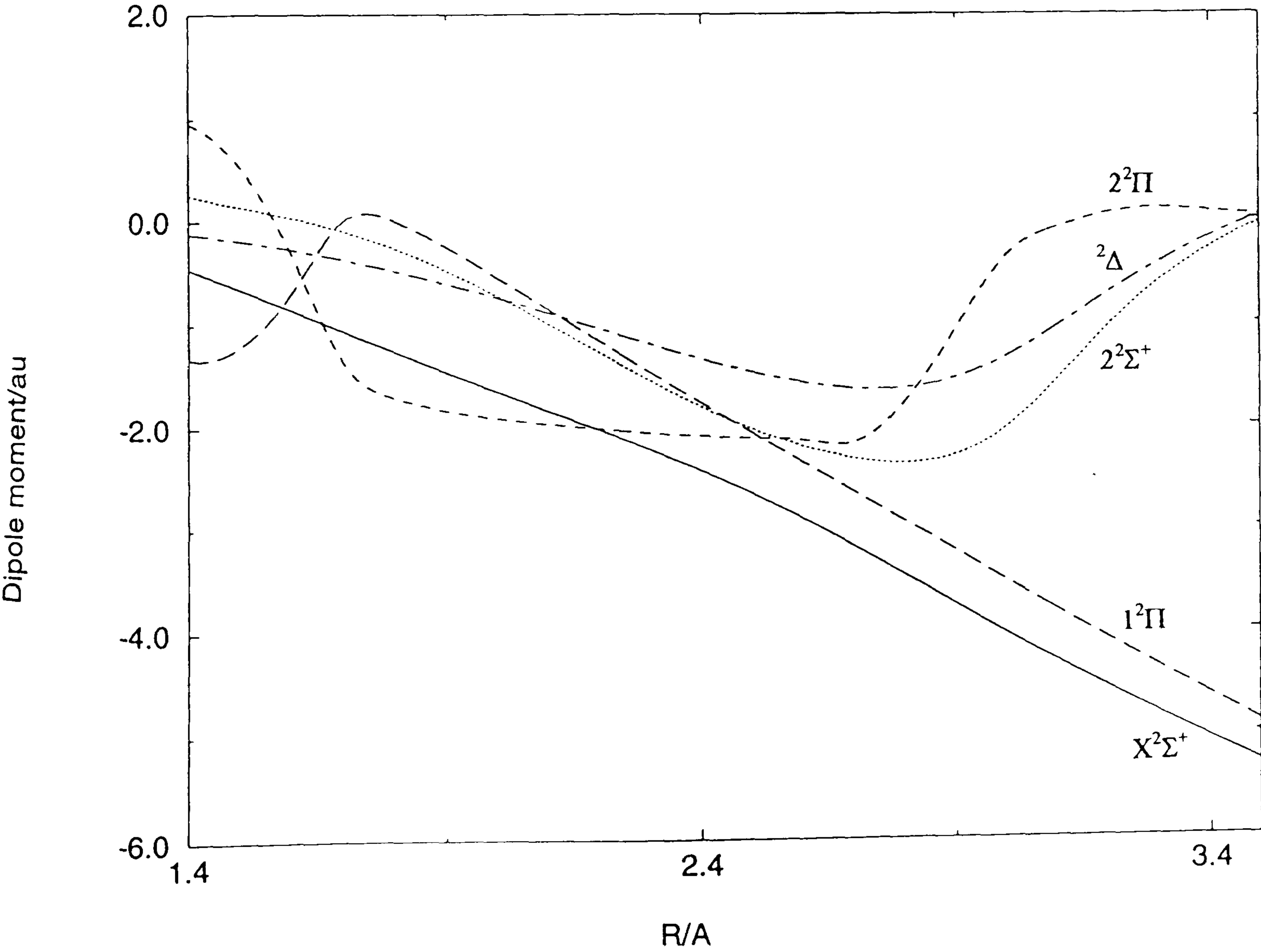
4.4.7 Dipole moments for the bound states of BBr⁺

Table 4.4.7 Dipole moment values

R/Å	X ² Σ ⁺	² Δ	2 ² Σ ⁺	1 ² Π	2 ² Π
1.4	-0.4553	-0.1179	0.2556	-1.3269	0.9514
1.5	-0.6482	-0.1804	0.1443	-1.2064	0.5368
1.6	-0.8497	-0.2618	0.0416	-0.6893	-0.3034
1.7	-1.0547	-0.3599	-0.0872	0.0106	-1.3516
1.8	-1.2591	-0.4732	-0.2580	0.0030	-1.7079
1.9	-1.4597	-0.6008	-0.4734	-0.2441	-1.8323
2.0	-1.6547	-0.7405	-0.7244	-0.5466	-1.9111
2.1	-1.8440	-0.8894	-0.9975	-0.8575	-1.9680
2.2	-2.0310	-1.0430	-1.2795	-1.1686	-2.0172
2.3	-2.2228	-1.1959	-1.5559	-1.4741	-2.0597
2.4	-2.4296	-1.3417	-1.8103	-1.7724	-2.0894
2.5	-2.6594	-1.4720	-2.0281	-2.0674	-2.1140
2.6	-2.9135	-1.5744	-2.1993	-2.3591	-2.1387
2.7	-3.1862	-1.6343	-2.3150	-2.6483	-2.1560
2.9	-3.7527	-1.5326	-2.2841	-3.2316	-1.0529
3.0	-4.0327	-1.3281	-2.0215	-3.5275	-0.3491
3.1	-4.3045	-1.0347	-1.5578	-3.8141	-0.0792
3.2	-4.5663	-0.7102	-1.0323	-4.0950	0.0592
3.5	-5.2876	0.0244	-0.0373	-4.9023	0.0314

Dipole moment/au

Figure 4.4.7 Electronic dipole moment functions



4.4.8 Electronic transition moments for BBr^+

Table 4.4.8 Transition moment values

$R/\text{\AA}$	$2^2\Sigma^+ \rightarrow X^2\Sigma^+$	$2^2\Pi \rightarrow X^2\Sigma^+$
1.4	0.1258	-0.3142
1.6	0.2526	-0.3928
1.8	0.3022	-0.3709
2.0	0.2667	-0.2867
2.2	0.2227	-0.2146
2.4	0.2480	-0.1547
2.6	0.3567	-0.1069
2.8	0.4862	-0.0680
3.0	0.5797	0.0335

Electronic transition moment/au

Figure 4.4.8 Electronic transition moments

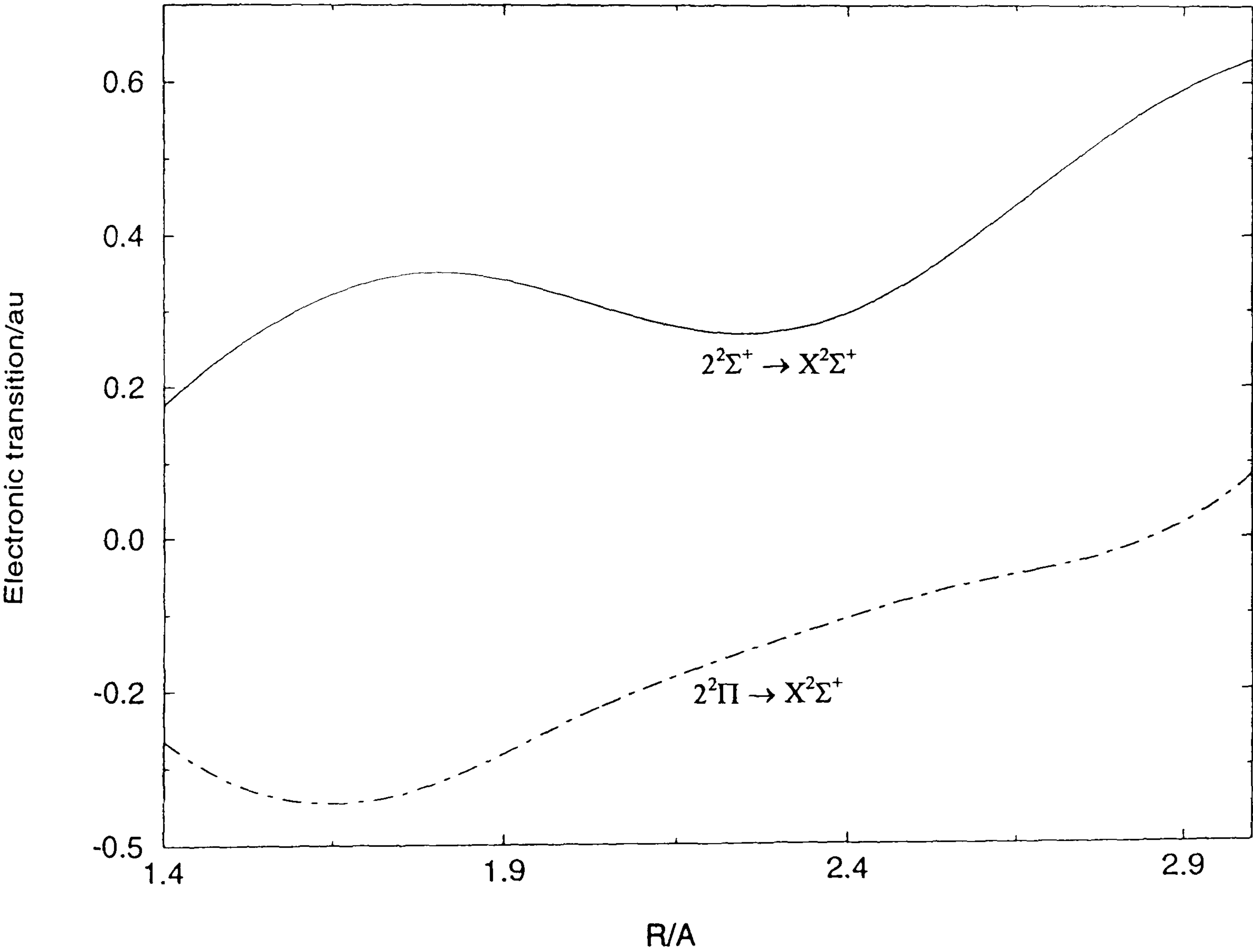


Figure 4.4.9 Calculated potential-energy curves for the doublet states of BBr^+

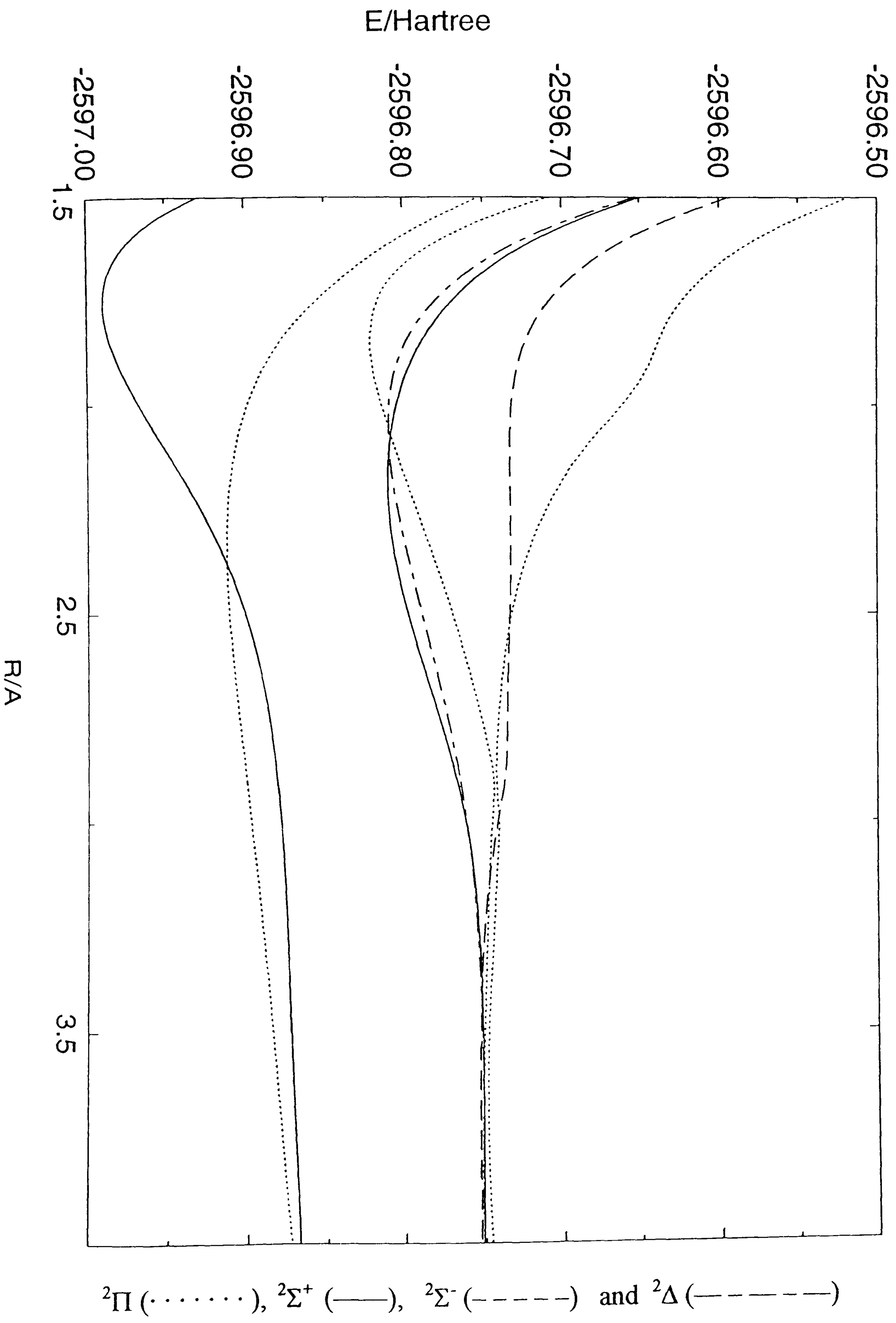


Figure 4.4.10 Calculated potential-energy curves for the quartet states of BBr^+

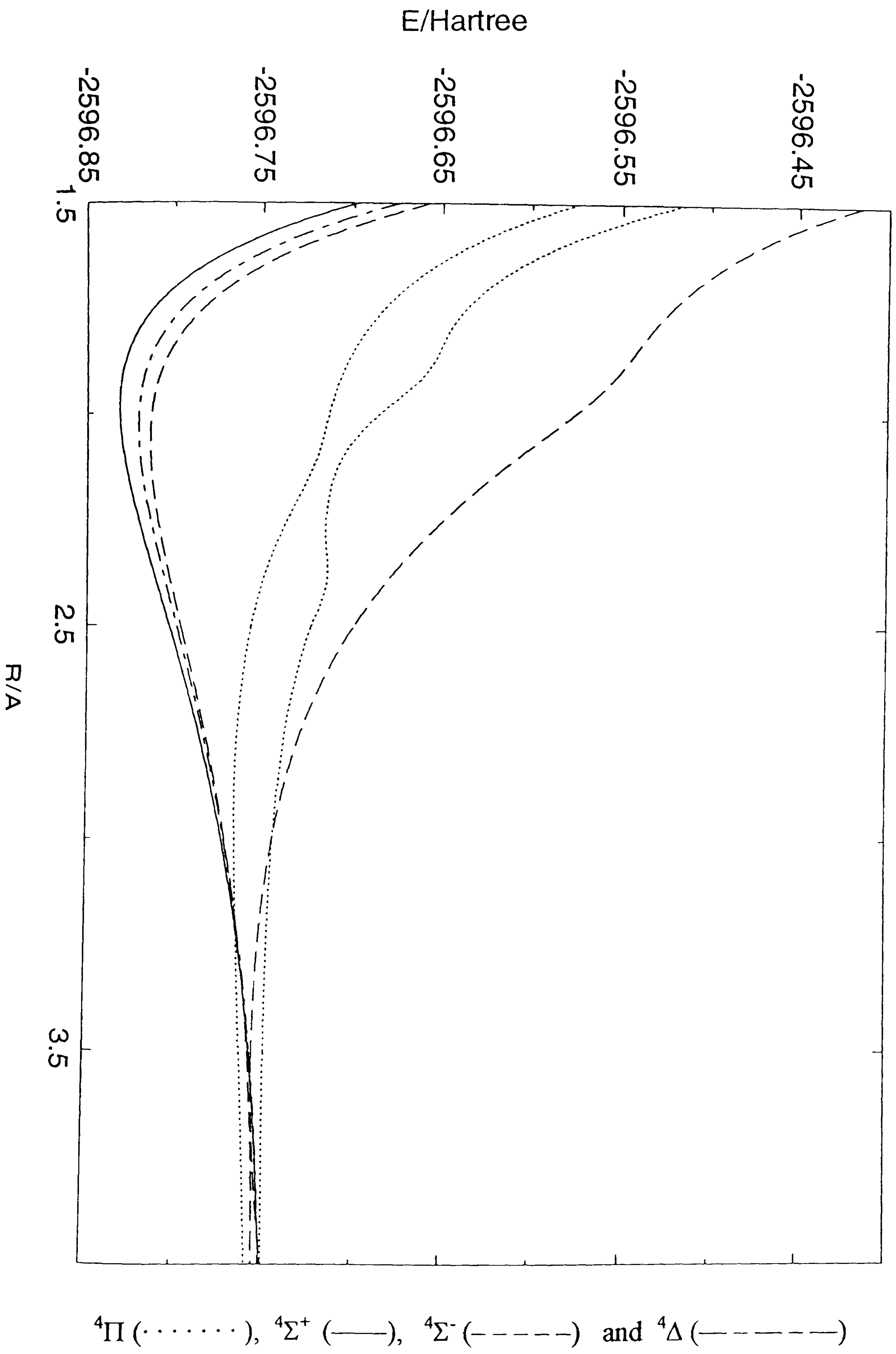


Table 4.4.9 Theoretical energy values for the $^1\Sigma^+$ state of BBr with the ANO basis sets [32]

R/Å	ROOT1	R/Å	ROOT1
1.0	2595.800953	2.4	2597.291327
1.1	2596.375862	2.5	2597.280179
1.2	2596.751270	2.6	2597.269149
1.3	2596.991422	2.7	2597.258434
1.4	2597.141808	2.8	2597.248181
1.5	2597.233414	2.9	2597.238499
1.6	2597.286857	3.0	2597.229471
1.7	2597.315676	3.1	2597.221152
1.8	2597.328715	3.2	2597.213575
1.9	2597.331768	3.5	2597.195371
2.0	2597.328629	4.0	2597.178831
2.1	2597.321747	4.5	2597.173118
2.2	2597.312653	5.0	2597.171358
2.3	2597.302300		

E/Hartree

Figure 4.4.11 Calculated potential energy curve for the $^1\Sigma^+$ state of BBr

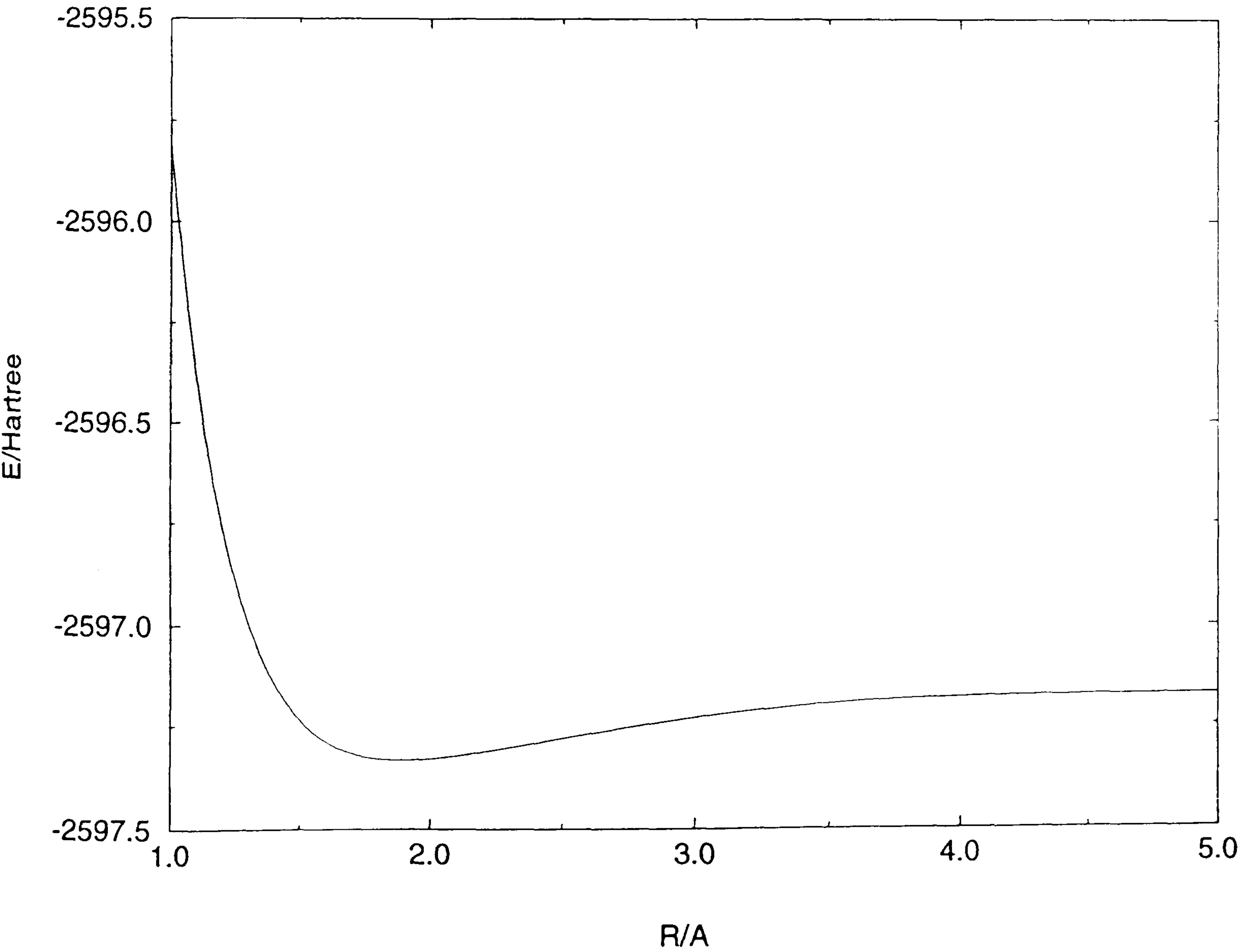


Table 4.1.4.7.A Spectroscopic constants for BBr⁺

	$r_e/\text{\AA}$	$E/\text{Hartree}^a$	T_e/eV	μ_e/au^b	ω_e/cm^{-1}	$\omega_{xe}/\text{cm}^{-1}$	B_0/cm^{-1}	B_1/cm^{-1}	B_2/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
1 ² Σ ⁺	1.755	-2596.989402	0	-1.1674	944.94	5.56	0.56408	0.55988	0.55563	0.56620	0.0042
					761.5 ^c	6.3 ^c					
1 ² Π	2.345	-2596.912023	2.1055	-1.6094	335.37	2.32	0.3612	0.3134	0.3101	0.3178	0.0030
		(-2596.856847)									
2 ² Π	1.845	-2596.820732	4.5895	-1.7753	791.76	7.84	0.5094	0.5044	0.4971	0.5128	0.0061
			2.501 ^c		813.8 ^c	7.5 ^c					
		(-2596.816706)									
2 ² Σ ⁺	2.180	-2596.810137	4.8778	-1.2230	476.08	0.017	0.3667	0.3663	0.3658	0.3669	0.0004
		(-2596.770981)									
² Δ	2.045	-2596.809671	4.8905	-0.8066	542.61	3.14	0.4140	0.4089	0.4049	0.4161	0.0046
		(-2596.781715)									
1 ² Σ ⁻	2.05	-2596.809567	4.8933	-0.7985	547.83	4.27	0.4133	0.4090	0.4047	0.4155	0.0043
		(-2596.781629)									
3 ² Π		-2596.624800									
4 ² Σ ⁺	1.985	-2596.831472	4.2973	-0.6253	597.97	4.30	0.4409	0.4364	0.4319	0.4431	0.0045
		(-2596.813127)									
⁴ Δ	2.030	-2596.820874	4.5856	-0.7432	554.23	4.09	0.4220	0.4176	0.4132	0.4242	0.0044
		(-2596.796975)									
1 ⁴ Σ ⁻	2.065	-2596.814169	4.7681	-0.8129	512.86	3.29	0.4073	0.4029	0.3983	0.4096	0.0044
		(-2596.785374)									
1 ⁴ Π		-2596.684653									
2 ⁴ Π		-2596.638300									
2 ⁴ Σ ⁻		-2596.524256									

^aEnergies in parentheses are vertical energies calculated at $r = 1.755 \text{ \AA}$ for the bound states described in the discussion.

^bWith respect to the centre of mass and with the direction BBr; $\text{au} = ea_0 \approx 8.4784 \times 10^{-30} \text{ Cm}$.

^cExperimental data [35].

4.2 Potential energy surfaces for HC + NO

The combustion reaction $\text{HC} + \text{NO}$ has been chosen. Also, CASSCF and CI calculations have been carried out with the VDZ basis sets for four states, namely $^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$ and $^3\Sigma^-$ for linear geometries, and $^1A'$ state for bent geometries.

For these calculations due to the computational difficulties some restrictions have been imposed on the possible configurations. The calculated energy values and the theoretical potential energy surfaces yielded from the calculations will be shown in section 4.2.1 which consists of two subsections 4.2.1.1 and 4.2.1.2 for linear geometries and bent geometries respectively. These calculations aimed to obtain potential energy surfaces for the reaction of HC with NO. However, we have only completed preliminary calculations because of lack of time. For collinear geometries we have found some discrepancies between calculations made for the C_s and C_{2v} symmetry. Our preliminary calculations show that for collinear geometries reaction is unlikely to occur whereas for non-collinear geometries reaction could occur without a barrier.

4.2.1 The results for HC + NO

As stated in the introduction, here we consider the combustion reaction $\text{HC} + \text{NO}$.

We present some preliminary calculations for the potential energy surfaces.

As before, for this system the MOLPRO suite of programs [156] has been used for the calculation of potential energy surfaces for $\text{HC} + \text{NO}$ using the correlation-consistent valence double-zeta (cc: vdz) basis sets devised by Dunning [157] and Woon and Dunning [158]. For the hydrogen atom the basis sets consisted of 4s functions contracted to 2s with the addition of a set of p functions and for C, N and O the sp

basis sets are composed of 9s4p functions contracted to 3s2p augmented with a set of d functions. Thus, the total number of contracted Gaussian basis functions was 47.

Two sets of calculations have been made for linear and bent geometries. This time, due to the computational difficulty some limitations have been imposed on the calculations. First, we have used the vdz basis mentioned above rather than the vqz basis sets we have used for the diatomic molecular ions. Second, we have treated the 2s-like electrons as core electrons in the CI calculations (for the CASSCF calculations we included the carbon 2s electrons in the active space).

As usual, for each spin and symmetry species molecular orbitals for subsequent CI calculations are obtained from state averaged CASSCF calculations [146,147]. For the linear structure the active space consisted of the valence orbitals $6a_1 - 10a_1, 1b_1 1b_2, 2b_1 2b_2, 3b_1 3b_2$ (for the CI calculations the valence orbitals are $7a_1 - 10a_1, 1b_1 1b_2, 2b_1 2b_2, 3b_1 3b_2$). For the bent structure the active orbitals are the valence orbitals $6a' - 13a', 1a'' - 3a''$ (for the CI calculations the valence orbitals are $7a' - 13a', 1a'' - 3a''$). CI calculations with the sets of reference configurations used in the CASSCF calculations were made with the internally contracted CI method of Knowles and Werner [150,151].

For the linear geometries, the calculations have been performed for four states, namely $^1\Sigma^+, ^1\Sigma^-, ^3\Sigma^+$ and $^3\Sigma^-$ under C_{2v} symmetry whereas for the bent geometry we have only calculated potential energy surfaces for the $^1A'$ states under C_s symmetry and the calculations for the other states are left for further work. In the case of the linear geometry all calculated energy values and theoretical potential energy surfaces for the four states are given in tables and figures 4.5.1 to 4.5.4 respectively and for the bent structure theoretical energy values and calculated potential surfaces are given in table

4.6.1 and figure 4.6.1 respectively. For the linear geometries the wavefunctions have been examined and assigned to Σ^+ (or Σ^-) and Δ states. For the linear and bent geometries details of the numbers of roots calculated (A), the sizes of the reference spaces (B), the numbers of contracted (C) and uncontracted (D) configurations are presented in table 4.2.1.

Table 4.2.1 Details of configuration interaction calculations

State	A	B	C	D
Linear				
$^1\Sigma^+$	2	4984	245712	4363128
$^1\Sigma^-$	2	4788	244284	4338432
$^3\Sigma^+$	2	7344	400804	7942166
$^3\Sigma^-$	2	7476	401200	7923618
Bent				
$^1A'$	2	9800	489404	8717534

4.2.1.1 The results for linear geometries with the VDZ basis sets

In the calculations for the linear structures we have taken the bond lengths for HC and NO as 1.058 Å and 1.198 Å respectively from the optimized linear geometry for HCNO reported by Pinnavaia et al.[77]. The C-N separation was then varied.

4.2.1.1.1 The CI calculations for the $^1\Sigma^+$ states of HC + NO

The calculated energy values, the potential energy curves and the dominant configurations, as the C-N distance is varied, are given in table 4.5.1, figure 4.5.1 and table 4.2.1.1.1 respectively.

Table 4.2.1.1.1 Dominant configurations for the $^1\Sigma^+$ state

State	Configuration	C-N separation
$^1\Sigma^+$	$\cdots 7a_1^2 1b_1^2 1b_2^2 2b_1^2 2b_2^2$	$1.0 \text{ Å} \leq r \leq 1.8 \text{ Å}$
	$\cdots 7a_1^2 8a_1^2 1b_1^2 1b_2^2 2b_1^2$	$r > 1.8 \text{ Å}$
$^1\Delta$	$\cdots 7a_1^2 1b_1^2 1b_2^2 2b_1^2 2b_2^1 3b_1^1$	$1.0 \text{ Å} \leq r \leq 1.6 \text{ Å}$
	$\cdots 7a_1^2 8a_1^2 1b_1^2 1b_2^2 2b_1^2$	$r \geq 1.7 \text{ Å}$

From table 4.5.1 and figure 4.5.1 roots 1 and 2 are a $^1\Delta$ and a $^1\Sigma^+$ state respectively.

4.2.1.1.2 The CI calculations for the $^1\Sigma^-$ states of HC + NO

The theoretical energies, the calculated potential energy surfaces and the dominant configurations are, in turn, to table 4.5.2, figure 4.5.2 and table 4.2.1.1.2.

As shown in figure 4.5.2 root1 is a $^1\Sigma^-$ state and root 2 is a $^1\Delta$ state.

Table 4.2.1.1.2 Dominant configurations for the $^1\Sigma^-$ state

State	Configuration	C-N separation
$^1\Sigma^-$	$\cdots 7a_1^2 1b_1^2 1b_2^2 2b_1^2 2b_2^1 3b_1^1$	$1.0 \text{ \AA} \leq r \leq 1.7 \text{ \AA}$
	$\cdots 7a_1^2 8a_1^2 1b_1^2 1b_2^2 2b_2^1 3b_1^1$	$r > 1.7 \text{ \AA}$

For the $^1\Delta$ state the dominant configuration was reported in table 4.2.1.1.1.

4.2.1.1.3 The CI calculations for the $^3\Sigma^+$ states of HC + NO

Table 4.5.3, figure 4.5.3 and table 4.2.1.1.3 show the calculated energy values, the theoretical potential energy surfaces and the dominant configurations respectively.

Table 4.2.1.1.3 Dominant configurations for the $^3\Sigma^+$ state

State	Configuration	Bond length
$^3\Sigma^+$	$\cdots 7a_1^2 1b_1^2 1b_2^2 2b_1^2 2b_2^1 3b_2^1$	$1.0 \text{ \AA} \leq r \leq 1.8 \text{ \AA}$
	$\cdots 7a_1^2 8a_1^2 1b_1^2 1b_2^2 2b_1^1 3b_1^1$	$r > 1.8 \text{ \AA}$
$^3\Delta$	$\cdots 7a_1^2 1b_1^2 1b_2^2 2b_1^2 2b_2^1 3b_2^1$	$1.0 \text{ \AA} \leq r < 1.8 \text{ \AA}$
	$\cdots 7a_1^2 8a_1^2 1b_1^2 1b_2^2 2b_1^1 3b_1^1$	$r \geq 1.8 \text{ \AA}$

From figure 4.5.3 root 1 is a $^3\Delta$ state and root 2 is a $^3\Sigma^+$ state.

4.2.1.1.4 The CI calculations for the $^3\Sigma^-$ states of HC + NO

The calculated energy values, the theoretical potential energy surfaces and the dominant configurations are presented in table 4.5.4, figure 4.5.4 and table 4.2.1.1.4 respectively.

Table 4.2.1.1.4 Dominant configurations for the $^3\Sigma^-$ state

State	Configuration	Bond length
$^3\Sigma^-$	$\cdots 7a_1^2 1b_1^2 1b_2^2 2b_1^2 2b_2^1 3b_1^1$	$1.0 \text{ \AA} \leq r < 1.8 \text{ \AA}$
	$\cdots 7a_1^2 8a_1^2 1b_1^2 1b_2^2 2b_1^1 2b_2^1$	$r \geq 1.8 \text{ \AA}$

Figure 4.5.4 shows that root1 is a $^3\Sigma^-$ state and root2 is a $^3\Delta$ state.

For the $^3\Delta$ state the dominant configuration was given in table 4.2.1.1.3.

4.2.1.2 The results for the bent geometry with the VDZ basis sets

For the calculations of the bent structure we have fixed the bond lengths for HC, CN and NO as 1.058 Å, 1.750 Å and 1.198 Å respectively. The CN distance of 1.75 Å was chosen so that we could investigate the variation of barrier height with the HCN angle.

4.2.1.2.1 The CI calculations for the $^1A'$ states of HC + NO

The aim of these calculations was to explore the potential energy surfaces for the attack of HC on NO and not to determine the structures of fulminic acid HCNO. However, there have been a number of theoretical studies of HCNO which we summarise briefly in the next section.

Table 4.6.1 and figure 4.6.1 give, in turn, the theoretical energy values and the calculated potential energy surfaces.

Here, we did not consider the electronic configurations because all three bond lengths are fixed and we are concerned the variation in energy value with angle.

4.2.1.3 General discussion for HC + NO

In the course of these calculations we encountered a problem that we did not have time to resolve. For collinear geometries the C_s calculations should yield the same results as the C_{2v} calculation. For reasons we do not understand we do not get this agreement.

Fulminic acid (HCNO) is thermodynamically known as the third most stable among the six CHNO isomers [77]. The major interest in previous work was to determine whether or not the equilibrium geometry is linear. Farnell *et al.* [161] made a calculation at the MP3 level using a 6-31G** basis set which took into account three values of the HNC angle of 160° , 170° and 180° with the other parameters optimized. They have found that the linear structure has the lowest energy with the 170° geometry being 22.6 cm^{-1} higher and suggested that the molecule was linear. Teles *et al.* [108] have, at the MP2/6-31G** level with full optimization, found that a bent structure (with a HNC angle of 150.1°) is higher than the optimized linear structure by $0.64\text{ kcal mol}^{-1}$. Recently, Nguyen, Pierloot and Vanquickenborne [162] have reinvestigated the equilibrium geometry of HCNO at the $MPn(n = 2-4)$, CISD and MCSCF levels using 6-31G**, 6-311G** and DZP basis sets with the full geometry optimization. Even though their best calculations suggest a bent equilibrium structure, they say that the energy difference between the linear and bent structure is too small for a definitive conclusion. Rendell, Lee and Lindh [163] have applied coupled cluster theory using a large basis set (CCSD(T)/TZ2P). Their incomplete results indicate that HCNO has a linear minimum structure. This is consistent with the earlier prediction of Bunker, Landsberg and Winnewisser [125], who used the semirigid bender model to

investigate the observed vibrations of this molecule. More recently, Pinnavaia *et al.* [77] have optimized the geometry at the MP2 level using the DZP, TZ2P and TZ2P + f basis sets and concluded that the linear structures are higher in energy than the bent ones by 0.95 kcal mol⁻¹ (~332 cm⁻¹) for DZP, 0.94 kcal mol⁻¹ (~329 cm⁻¹) for TZ2P and 0.28 kcal mol⁻¹ (~98 cm⁻¹) for TZ2P + f.

Figures 4.5.5 and 4.5.6 present the calculated potential energy surfaces for the singlet and triplet states respectively. The kinetics of the reaction of CH with NO have been investigated by Bocherel *et al.* [74] who found that the reaction is very fast. The rate constant at 298 K is $(1.98 \pm 0.2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. Over the temperature range 13-708 K the unweighted mean of the rate constant is $(1.9 \pm 0.7) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. They concluded that the rate constant is determined by capture by the long-range part of the monotonically attractive potential energy surface. From figures 4.5.5. and 4.5.6 it can be seen that our calculations for the collinear approach of HC to NO all have potential barriers. The smallest is on the ¹Σ⁺ surface for which the potential barrier is about 238 kJ mol⁻¹. It thus seems unlikely that reaction will occur for collinear geometries.

From the preliminary calculations we have made for a CN distance of 1.75 Å, it would appear that as the HCN angle decreases, the energy decreases to values below that for HC + NO at a CN distance of 5 Å. Thus, it seems plausible that reaction could occur without a barrier for non-collinear approach of HC to NO. We were not able to pursue this further because of lack of time.

4.5.1 The CI results(VDZ) of the $^1\Sigma^+$ states for HC + NO with the linear geometry

Table 4.5.1 Theoretical energy values

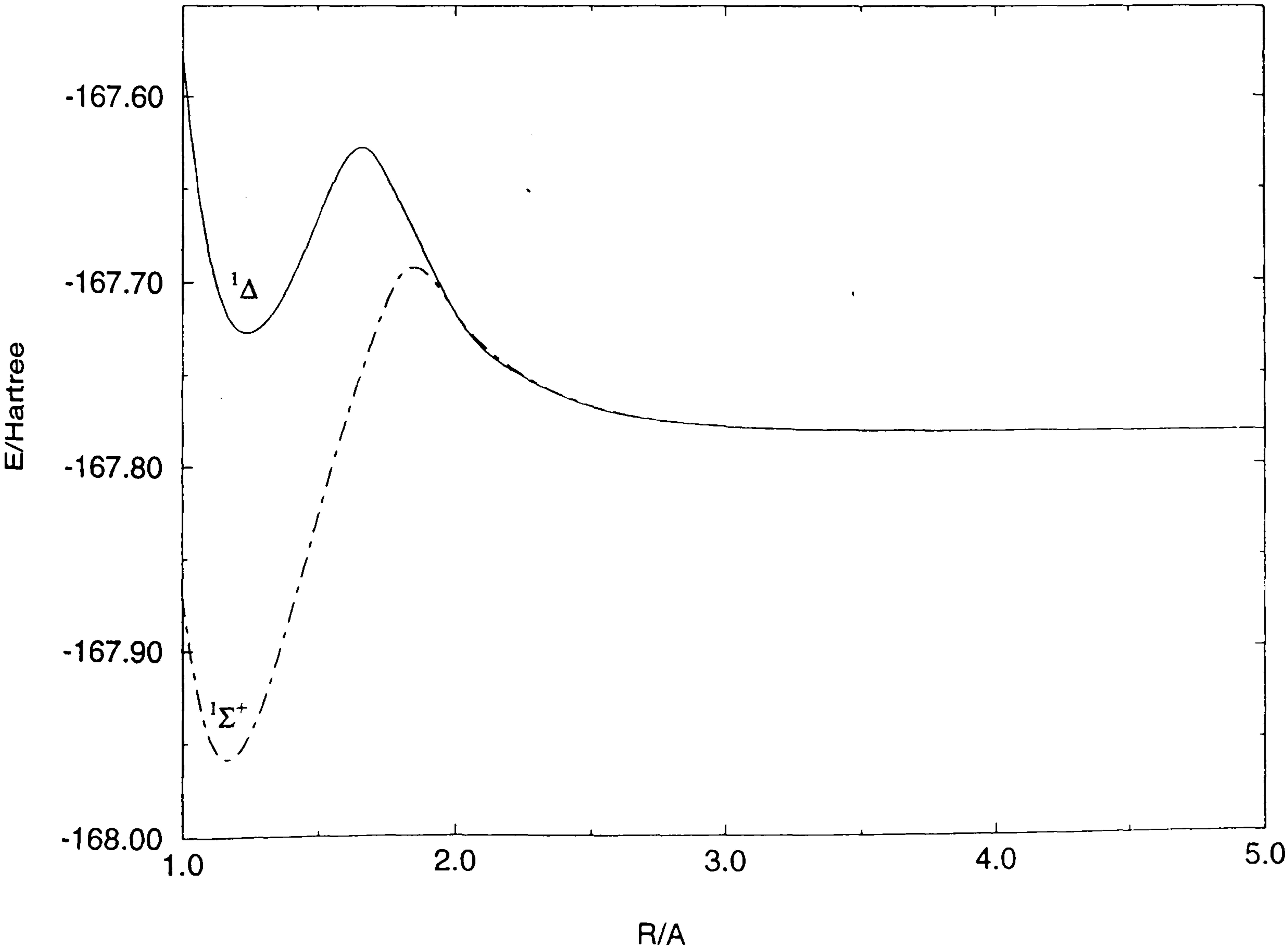
R/Å	ROOT1	ROOT2
1.00	-167.575132	-167.869724
1.10	-167.686149	-167.947784
1.20	-167.724532	-167.955854
1.25	-167.726631	-167.944058
1.50	-167.665897	-167.826500
1.60	-167.634715	-167.776254
1.70	-167.630100	-167.731718
1.75	-167.642321	-167.712147
1.80	-167.656720	-167.696886
2.00	-167.716721	-167.716353
2.25	-167.751434	-167.750352
2.50	-167.767808	-167.767125
2.75	-167.775439	-167.775021
3.00	-167.778879	-167.778614
3.50	-167.781114	-167.780995
4.00	-167.781581	-167.781520
4.50	-167.781670	-167.781636
5.00	-167.781719	-167.781699

$^1\Delta$

$^1\Sigma^+$

E/Hartree

Figure 4.5.1 Calculated potential energy surfaces

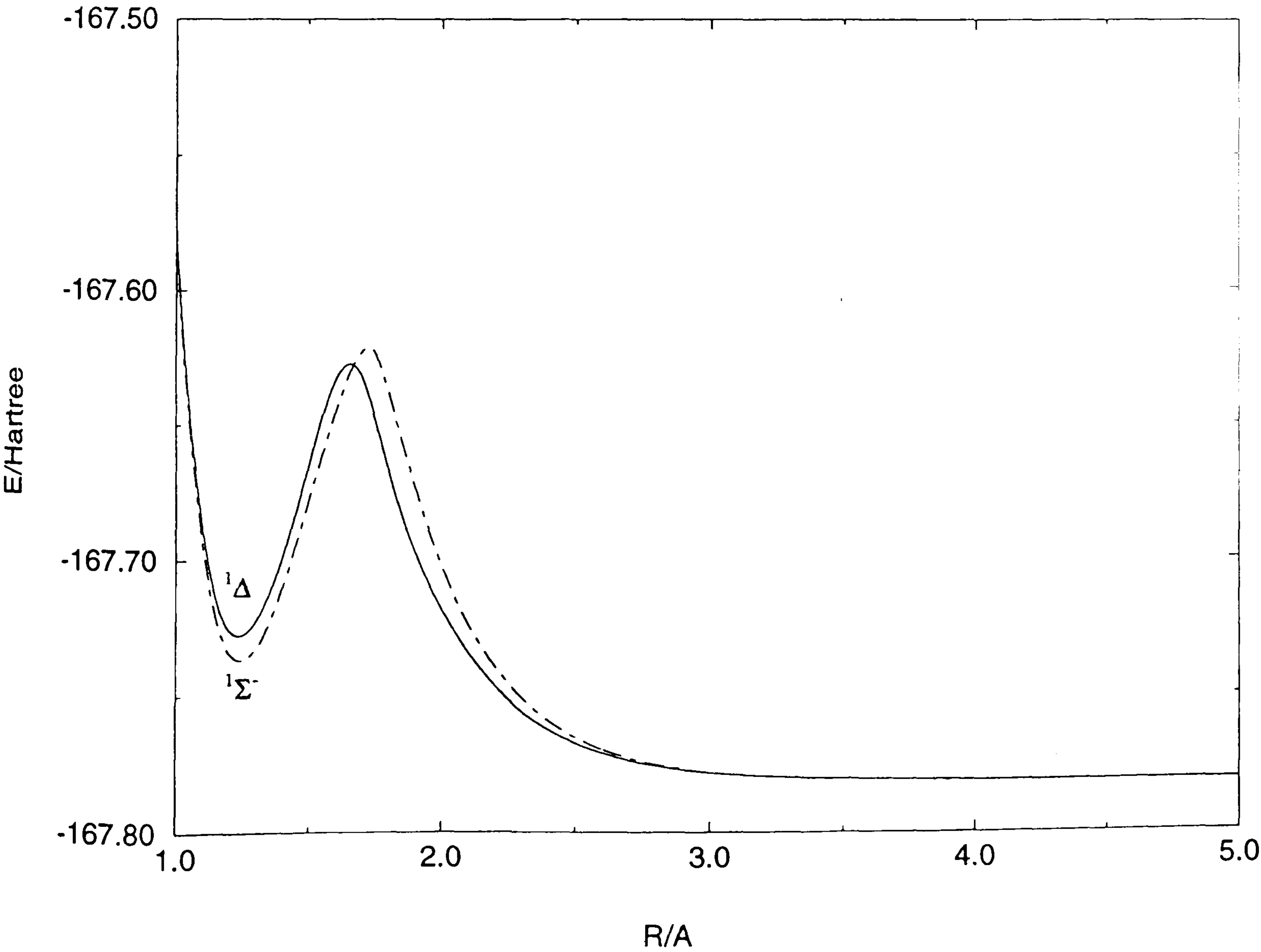


4.5.2 The CI results(VDZ) of the $^1\Sigma^-$ states for HC + NO with the linear geometry

Table 4.5.2 Theoretical energy values

R/Å	ROOT1	ROOT2
1.00	-167.579838	-167.576162
1.10	-167.692781	-167.686831
1.20	-167.733383	-167.725105
1.25	-167.736519	-167.727136
1.50	-167.678289	-167.665521
1.60	-167.646361	-167.634129
1.70	-167.622683	-167.631130
1.75	-167.622652	-167.646788
1.80	-167.637496	-167.665854
2.00	-167.701497	-167.717491
2.25	-167.745044	-167.751182
2.50	-167.765502	-167.767695
2.75	-167.774688	-167.775401
3.00	-167.778691	-167.778870
3.50	-167.781167	-167.781114
4.00	-167.781631	-167.781579
4.50	-167.781703	-167.781670
5.00	-167.781738	-167.781718
	$^1\Sigma^-$	$^1\Delta$
E/Hartree		

Figure 4.5.2 Calculated potential energy surfaces



4.5.3 The CI results(VDZ) of the $^3\Sigma^+$ states for HC + NO with the linear geometry

Table 4.5.3 Theoretical energy values

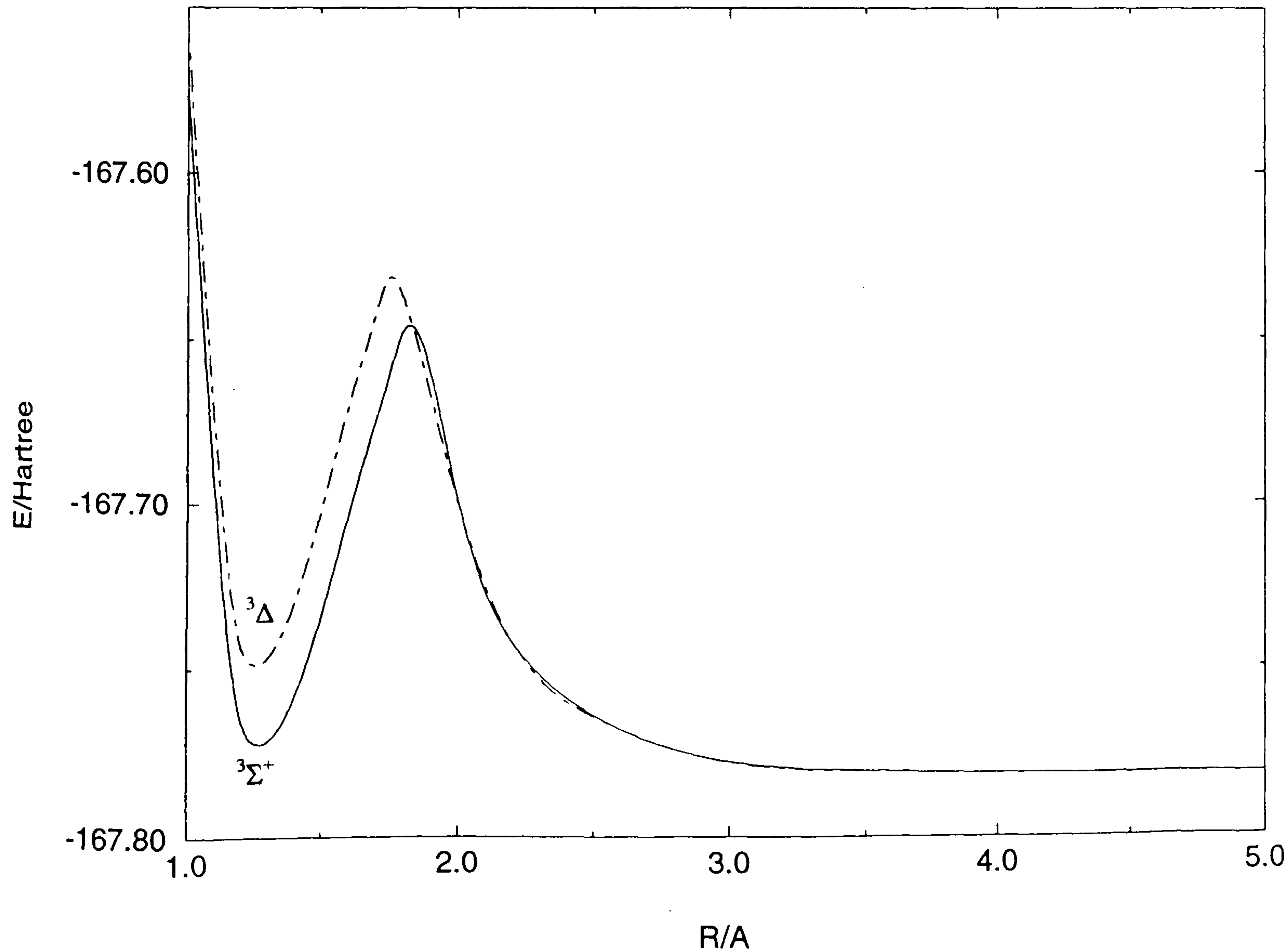
R/Å	ROOT1	ROOT2
1.00	-167.555214	-167.571886
1.10	-167.672814	-167.692539
1.20	-167.741654	-167.764179
1.25	-167.748339	-167.772093
1.50	-167.703000	-167.734342
1.60	-167.670809	-167.703971
1.70	-167.642313	-167.674672
1.75	-167.631254	-167.660634
1.80	-167.637330	-167.647509
2.00	-167.699254	-167.698262
2.25	-167.747766	-167.747006
2.50	-167.764383	-167.763861
3.00	-167.778208	-167.777969
3.50	-167.780944	-167.780829
4.00	-167.781502	-167.781443
4.50	-167.781608	-167.781574
5.00	-167.781657	-167.781637

$^3\Delta$

$^3\Sigma^+$

E/Hartree

Figure 4.5.3 Calculated potential energy surfaces



4.5.4 The CI results(VDZ) of the $^3\Sigma^-$ states for HC + NO with the linear geometry

Table 4.5.4 Theoretical energy values

R/Å	ROOT1	ROOT2
1.00	-167.542559	-167.555479
1.10	-167.673590	-167.689100
1.20	-167.726664	-167.744237
1.25	-167.738339	-167.757069
1.50	-167.682789	-167.703484
1.60	-167.652668	-167.671658
1.75	-167.660877	-167.631198
2.00	-167.723246	-167.702236
2.25	-167.752516	-167.743374
2.50	-167.773120	-167.769460
3.00	-167.784537	-167.783814
3.50	-167.786844	-167.786656
4.00	-167.787252	-167.787182
4.50	-167.787291	-167.787257
5.00	-167.787307	-167.787287

$^3\Sigma^-$

$^3\Delta$

E/Hartree

Figure 4.5.4 Calculated potential energy surfaces

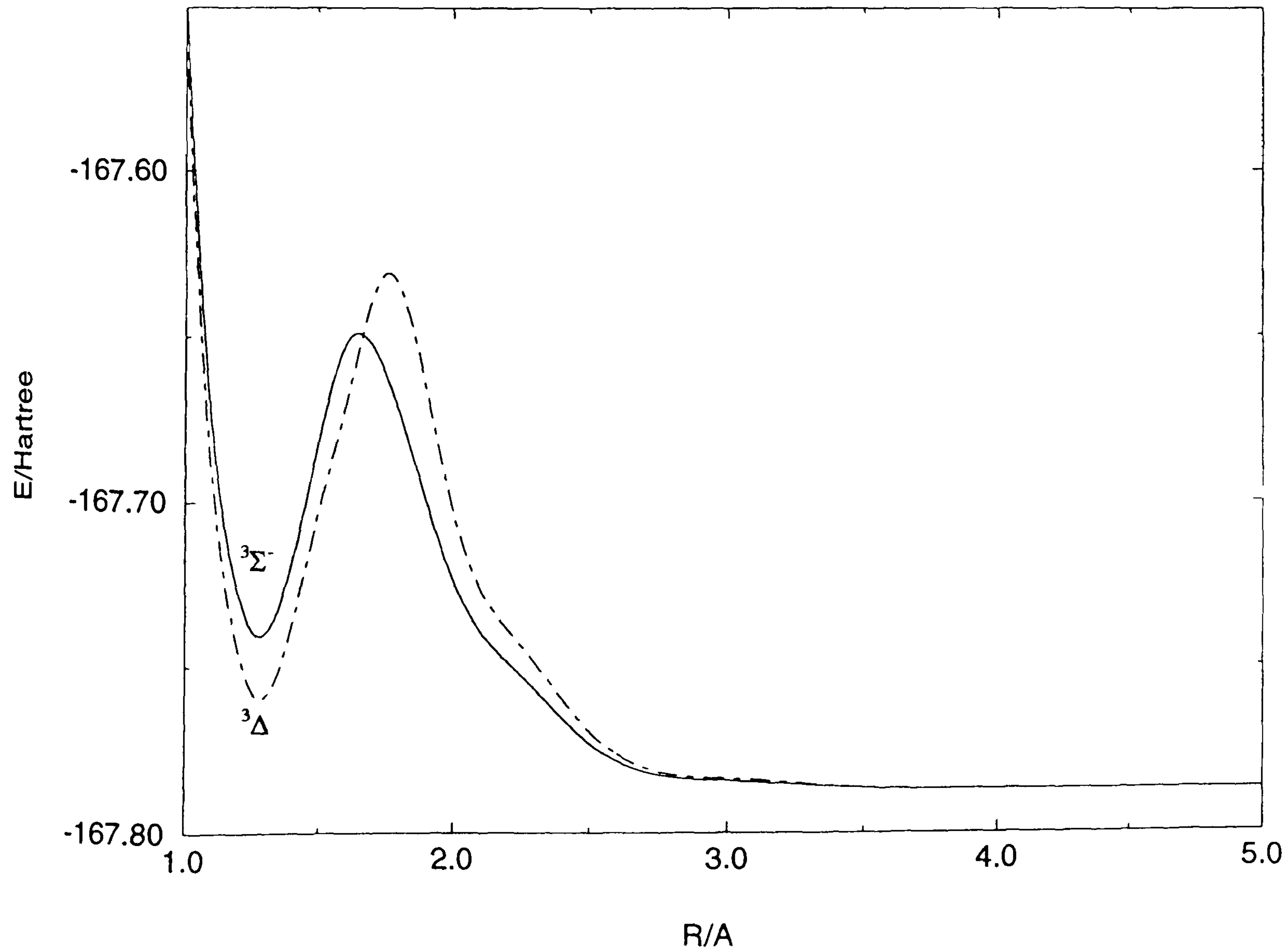


Figure 4.5.5 Calculated potential energy surfaces of the singlet states for HC + NO

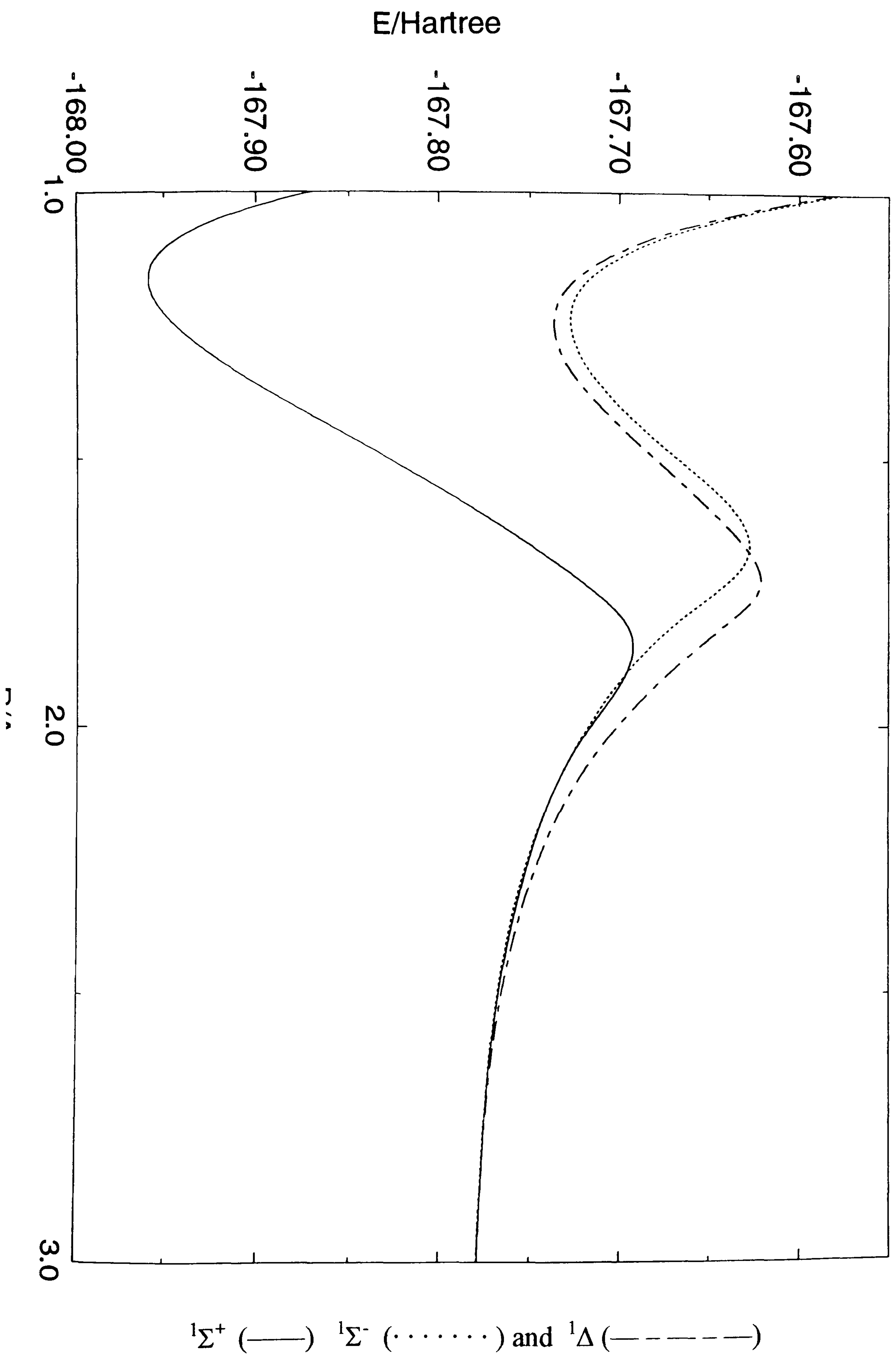
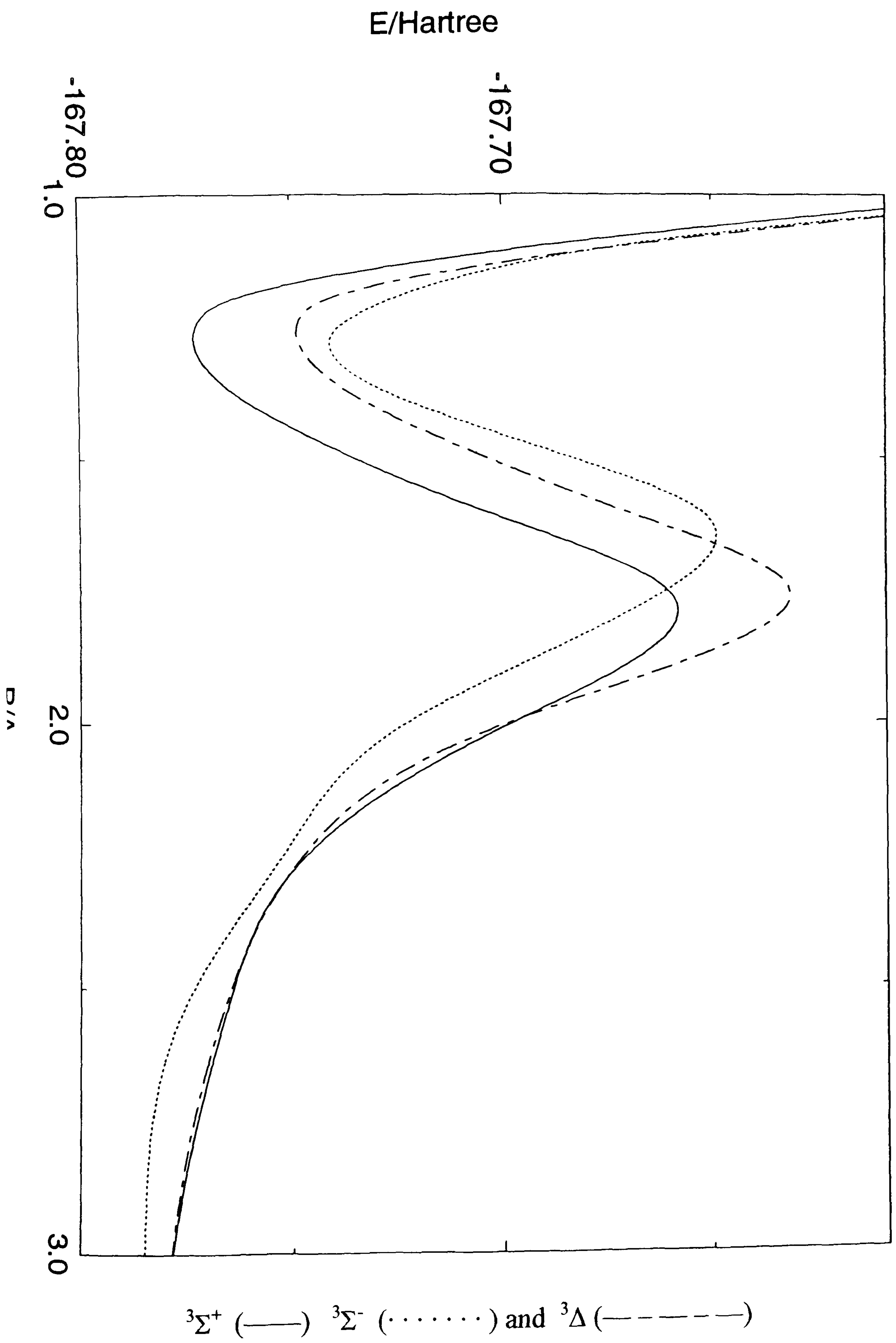


Figure 4.5.6 Calculated potential energy surfaces of the triplet states for HC + NO



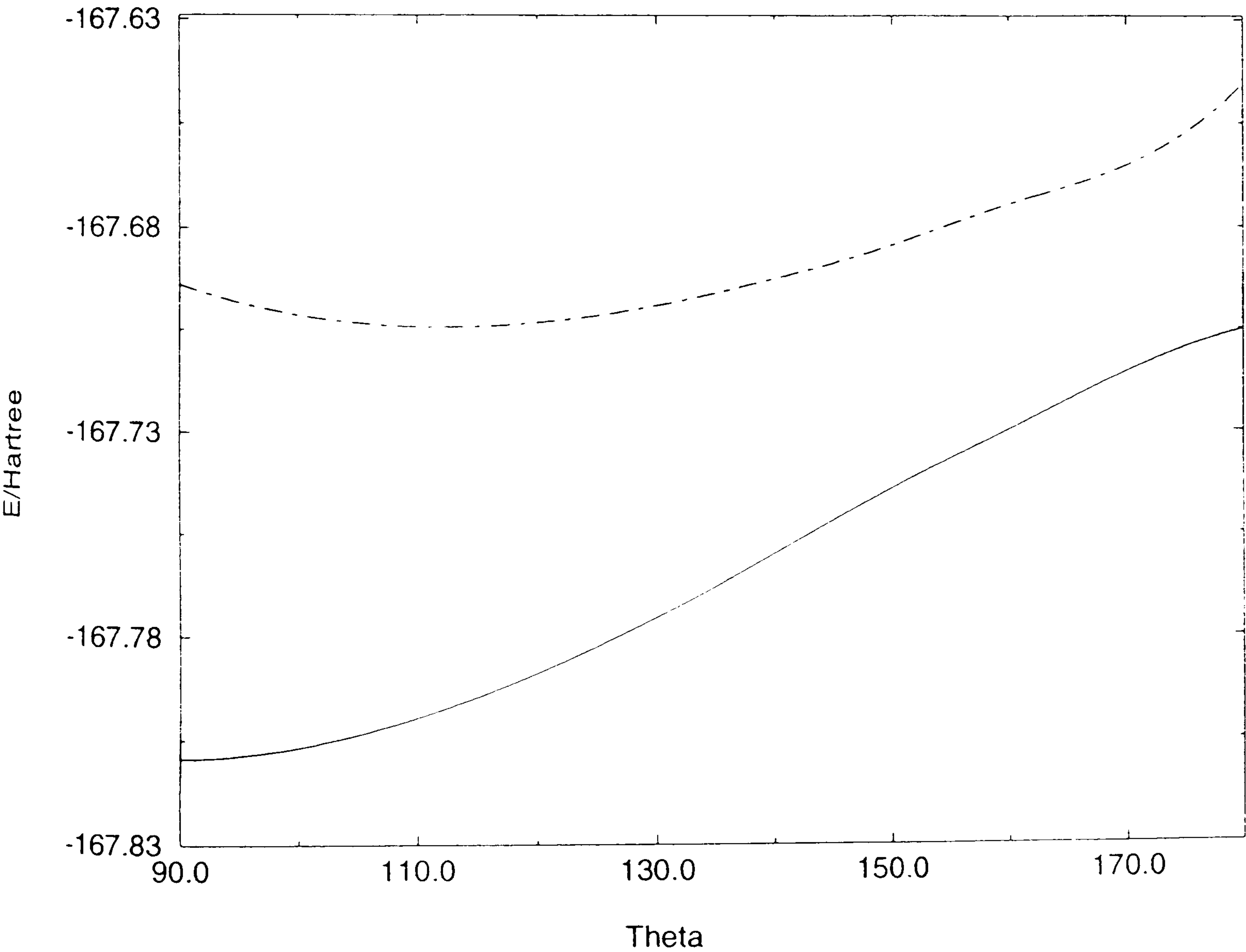
4.6.1 The CI results (VDZ) of the ¹A' states for HC + NO with the bent geometry

Table 4 6 1 Theoretical energy values

THETA	ROOT1	ROOT2
180.0	-167.702189	-167.642547
170.0	-167.712648	-167.662290
160.0	-167.726886	-167.671653
150.0	-167.741266	-167.681587
140.0	-167.757073	-167.689732
130.0	-167.772361	-167.696202
120.0	-167.785808	-167.700328
110.0	-167.796492	-167.701317
100.0	-167.803633	-167.698459
90.0	-167.806392	-167.691075

E/Hartree

Figure 4.6.1 Calculated potential energy surfaces



θ = CNO angle (180°) and all the distances (HC, CN and NO) are fixed.
Only the HCN angle is varied.

5. Summary

This thesis provides information about electronic configurations and spectroscopic constants derived from calculated potential energy curves for the diatomic molecular ions NF^+ , PCl^+ , AsCl^+ and BBr^+ and some preliminary calculations of potential energy surfaces for the reaction of CH with NO.

5.1 Potential energy curves for diatomic molecular ions

Our work generated potential energy curves for the low-lying electronic states of the molecular ions NF^+ , PCl^+ , AsCl^+ and BBr^+ correlating with the lowest dissociation asymptotes, namely $\text{N}^+(^3\text{P})+\text{F}(^2\text{P})$, $\text{P}^+(^3\text{P})+\text{Cl}(^2\text{P})$, $\text{As}^+(^3\text{P})+\text{Cl}(^2\text{P})$, $\text{B}^+(^1\text{S})+\text{Br}(^2\text{P})$ and $\text{B}(^2\text{P})+\text{Br}^+(^3\text{P})$.

The Wigner-Witmer correlation rules give the following states for the dissociation asymptotes considered.

For NF^+ , PCl^+ and AsCl^+ $^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Pi(2)$, $^4\Delta$.

For BBr^+ $^2\Sigma^+$, $^2\Pi$ from $\text{B}^+(^1\text{S})+\text{Br}(^2\text{P})$ and $^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Pi(2)$, $^4\Delta$ from $\text{B}(^2\text{P})+\text{Br}^+(^3\text{P})$.

CASSCF and CI calculations have been made using the correlation-consistent valence quadruple-zeta (VQZ) basis sets for NF^+ , PCl^+ and averaged atomic natural orbital (ANO) basis sets for AsCl^+ , BBr^+ .

The aim of calculations is to obtain spectroscopic constants for bound states from the ro-vibrational energy levels calculated from the potential energy curves. These

calculated values are useful predictions for electronic states which have not been observed.

For NF^+ there are only four bound states ($\text{X}^2\Pi$, $\text{A}^2\Pi$, $1^4\Sigma^-$, $1^4\Pi$).

Spectroscopic constants for the $\text{X}^2\Pi$ state have been obtained experimentally [7].

Calculated constants ω_e and R_e differ from the experimental values by 2.7 % and 0.42 % and previous theoretical values [57] by 4.1 % and 0.25 %.

There is a reasonable agreement between calculated value $\omega_e\chi_e$ (13.80 cm^{-1}) and experimental value ($10 \pm 6 \text{ cm}^{-1}$).

The calculations also include transition moments for bound-bound transitions.

For PCl^+ only four states ($\text{X}^2\Pi$, $\text{A}^2\Pi$, $1^4\Sigma^-$, $1^4\Pi$) are bound.

There are experimental spectroscopic constants for $\text{X}^2\Pi$ and $\text{A}^2\Pi$ states[8,9].

In the case of $\text{X}^2\Pi$ state, the calculated vibrational constant(ω_e), anharmonicity constant($\omega_e\chi_e$), rotational constant(B_e), vibration-rotation constant(α_e) and bond length(R_e) from this work differ from the experimental values[8,9] by 1.23 %, 1.15 %, 1.41 %, 3.40 % and 0.79 %. Thus, theoretical values are in very good agreement with experimental values. In the case of the weakly bound $\text{A}^2\Pi$ state, the vibrational constant(ω_e), rotational constant(B_0), rotational constant(B_1), bond length(R_e) are in reasonable agreement with the experimental data[1] with the errors of 2.43 %, 2.66 %, 3.21 % and 1.33 %.

For AsCl^+ only four states ($X^2\Pi$, $A^2\Pi$, $1^4\Sigma^-$, $1^4\Pi$) are bound.

For AsCl^+ two states ($X^2\Pi$, $A^2\Pi$) have been observed [33].

The errors between the calculated values ω_e , $\omega_e\chi_e$, B_e , α_e and R_e for $X^2\Pi$ and experimental values [33] are 1.44 %, 7.17 %, 2.13 %, 2.99 % and 1.18 %.

For the $A^2\Pi$ state, errors of 2.70 %, 2.73 % and 1.28 % between the theoretical values of B_0 , B_1 and R_e and experimental values [33] exist. The $1^4\Sigma^-$ and $1^4\Pi$ states are also bound and constants have been calculated for those states and are predictions for the experimental parameters.

For BBr^+ there are many bound states calculated, namely $X^2\Sigma^+$, $2^2\Sigma^+$, $^2\Delta$, $A^2\Pi$, $2^2\Pi$, $1^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$, $^4\Delta$. Spectroscopic constants are calculated but are in poor agreement with the experimental values ($X^2\Sigma^+$ and $2^2\Pi$) [35]. To confirm our results a comparable calculation for the ground state ($X^1\Sigma^+$) of neutral BBr has been made in the same way as for the calculations for BBr^+ . From the potential-energy curve the theoretical values of $\omega_e=697.3\text{cm}^{-1}$ and $B_e=0.488\text{cm}^{-1}$ have been computed and agree well with the experimental values [160] ($\omega_e=687.3\text{cm}^{-1}$ and $B_e=0.48918\text{cm}^{-1}$). Our values differ from the experimental values by 1.45% and 0.2%. Thus, theoretical values are in very good agreement with the experimental values and we are confident about the accuracy of our results for BBr^+ .

It is suggested that the spectrum of BBr^+ should be reinvestigated.

5.2 Potential energy surfaces for HC + NO

The reaction of CH with NO gives a number of possible exothermic reaction channels [74] which are $\text{CH} + \text{NO} \rightarrow \text{CO} + \text{NH}$ ($\Delta H_{298K}^{\circ} = -439 \text{ kJ mol}^{-1}$), $\text{CN} + \text{OH}$ (-188 kJ mol^{-1}), $\text{HCN} + \text{O}$ (-301 kJ mol^{-1}), $\text{HCO} + \text{N}$ (-184 kJ mol^{-1}) and $\text{NCO} + \text{H}$ (-335 kJ mol^{-1}). We considered here the entrance channel for CH + NO.

CASSCF and CI calculations have been made with the VDZ basis sets. Calculations are limited to $^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$ and $^3\Sigma^-$ states for the linear geometries and to $^1A'$ states for a bent structure. Our calculations meant to explore reaction mechanisms, transition states, reaction intermediates and rate constants from the reaction of HC with NO but due to lack of time we were only able to make preliminary calculations. For collinear structures the results should be the same for C_s and C_{2v} symmetries but we encountered some discrepancies that we could not understand. For the collinear approach of HC to NO it seems unlikely that reaction will occur because the potential barrier for the $^1\Sigma^+$ state is about 238 kJ mol^{-1} . However, for non-collinear approach of HC to NO it seems possible that reaction will occur without a barrier because the energy value is lower than that for HC + NO at a CN distance of 5 Å. Due to lack of time we could not pursue this further.

6. Conclusions

For NF^+ , PCl^+ , AsCl^+ and BBr^+ , theoretical values are in reasonably good agreement with experimental data where available.

For states which have not been observed our theoretical values should be reasonable predictions of the experimental values.

Theoretical values can provide information which is important or difficult to obtain experimentally.

Our preliminary results for $\text{HC} + \text{NO}$ suggest that reaction is unlikely to occur for collinear geometries but for non-collinear geometries reaction may occur without a barrier.

Appendices

Appendix A

As mentioned earlier in Chapter 3, the input files of NF^+ , PCl^+ , AsCl^+ and BBr^+ are presented for the MCSCF calculations. Four species each have the six input files which correspond to the $^2\Pi$, $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^-$, $^4\Sigma^+$ and $^4\Pi$ states respectively. For the CI calculations the input files for four species have not been considered because the wavefunctions on the WF cards are defined as in the MCSCF calculations.

A.1 The input files for NF^+

***, The MCSCF (CASSCF) calculation for the NF^+ excited states

file,2,nfplus.wfu,new

zmat,angstrom

N

F,N,r

endz

basis=vqz (vdz or vtz)

r=1.1

int;

1) The input file for the $^2\Pi$ state

rhf;wf,15,2,1;

text,CASSCF, state averaged orbitals for 2Π states

multi;occ,6,2,2;closed,2,0,0;start,2130.2;orbital,2140.2;natorb,,ci;

wf,15,2,1;state,2;wf,15,3,1;state,2;maxiter,15;

ci;wf,15,2,1;state,2;

2) The input file for the $^2\Sigma^+$ state

rhf;wf,15,1,1;

text,CASSCF, state averaged orbitals for $2\Sigma^+$ states

multi;occ,6,2,2;closed,2,0,0;start,2130.2;orbital,2140.2;natorb,,ci;

wf,15,1,1;state,5;maxiter,15;

ci;wf,15,1,1;state,5;

3) The input file for the $^2\Sigma^-$ state

```
rhf,wf,15,4,1;  
text,CASSCF, state averaged orbitals for 2SIG- states  
multi;occ,6,2,2;closed,2,0,0;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,15,4,1;state,5;maxiter,15;  
ci;wf,15,4,1;state,5;  
---
```

4) The input file for the $^4\Sigma^-$ state

```
rhf,wf,15,4,3;  
text,CASSCF, state averaged orbitals for 4SIG- states  
multi;occ,6,2,2;closed,2,0,0;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,15,4,3;state,3;maxiter,15;  
ci;wf,15,4,3;state,3;  
---
```

5) The input file for the $^4\Sigma^+$ state

```
rhf,wf,15,1,3;  
text,CASSCF, state averaged orbitals for 4SIG+ states  
multi;occ,6,2,2;closed,2,0,0;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,15,1,3;state,5;maxiter,15;  
ci;wf,15,1,3;state,5;  
---
```

6) The input file for the $^4\Pi$ state

```
rhf,wf,15,2,3;  
text,CASSCF, state averaged orbitals for 4PI states  
multi;occ,6,2,2;closed,2,0,0;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,15,2,3;state,2;wf,15,3,3;state,2;maxiter,15;  
ci;wf,15,2,3;state,2;  
---
```

A.2 The input files for PCI^+

***, The MCSCF(CASSCF) for the PCI^+ excited states

```
file,2,pclplus.wfu,new
```

```
zmat,angstrom
```

```
p
```

```
cl,p,r
```

```
endz
```

```
basis=vqz (vdz or vtz)
```

```
r=2.0
```

```
int;
```

1) The input file for the $^2\Pi$ state

```
rhf,wf,31,2,1;  
text,CASSCF, state averaged orbitals for  $\Pi$  states  
multi;occ,10,4,4;closed,6,2,2;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,31,2,1;state,2;wf,31,3,1;state,2;maxiter,15;  
ci,wf,31,2,1;state,2;  
---
```

2) The input file for the $^2\Sigma^+$ state

```
rhf,wf,31,1,1;  
text,CASSCF, state averaged orbitals for  $2\Sigma^+$  states  
multi;occ,10,4,4;closed,6,2,2;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,31,1,1;state,2;maxiter,15;  
ci,wf,31,1,1;state,2;  
---
```

3) The input file for the $^2\Sigma^-$ state

```
rhf,wf,31,4,1;  
text,CASSCF, state averaged orbitals for  $2\Sigma^-$  states  
multi;occ,10,4,4;closed,6,2,2;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,31,4,1;state,5;maxiter,15;  
ci,wf,31,4,1;state,5;  
---
```

4) The input file for the $^4\Sigma^-$ state

```
rhf,wf,31,4,3;  
text,CASSCF, state averaged orbitals for  $4\Sigma^-$  states  
multi;occ,10,4,4;closed,6,2,2;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,31,4,3;state,3;maxiter,15;  
ci,wf,31,4,3;state,3;  
---
```

5) The input file for the $^4\Sigma^+$ state

```
rhf,wf,31,1,3;  
text,CASSCF, state averaged orbitals for  $4\Sigma^+$  states  
multi;occ,10,4,4;closed,6,2,2;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,31,1,3;state,2;maxiter,15;  
ci,wf,31,1,3;state,2;  
---
```

6) The input file for the $^4\Pi$ state

```
rhf,wf,31,2,3;  
text,CASSCF, state averaged orbitals for  $4\Pi$  states  
multi;occ,10,4,4;closed,6,2,2;start,2130.2;orbital,2140.2;natorb,,ci;  
wf,31,2,3;state,2;wf,31,3,3;state,2;maxiter,15;  
ci,wf,31,2,3;state,2;  
---
```


A.3 The input files for AsCl⁺

The input files are divided into two cases, depending on which basis set we have used.

A.3.1 The input files for AsCl⁺ with effective core potentials (ECP)

*****, The MCSCF(CASSCF) with ECP for the AsCl⁺ excited states**

file,2,asclplus.wfu,new

zmat,angstrom

as

cl,as,r

endz

r=2.0

int;

ecp,1,ecp28mwb;

sp,1,ECP28mwb;c;

d,1,0.2;

spd,2,vqz(vdz or vtz);c

1) The input file for the ²Π state

rhf,wf,21,2,1;save,2130.2;

text,CASSCF, state averaged orbitals for 2Π states

multi,start,2130.2;orbital,2140.2;wf,21,2,1;state,2;wf,21,3,1;state,2;maxiter,20;

ci,maxiter,30;wf,21,2,1;state,2;

2) The input file for the ²Σ⁺ state

rhf,wf,21,1,1;save,2130.2;

text,CASSCF, state averaged orbitals for 2Σ⁺ states

multi,start,2130.2;orbital,2140.2;wf,21,1,1;state,2;maxiter,20;

ci,maxiter,30;wf,21,1,1;state,2;

3) The input file for the ²Σ⁻ state

rhf,wf,21,4,1;save,2130.2;

text,CASSCF, state averaged orbitals for 2Σ⁻ states

multi,start,2130.2;orbital,2140.2;wf,21,4,1;state,3;maxiter,20;

ci,maxiter,30;wf,21,4,1;state,3;

4) The input file for the $^4\Sigma^-$ state

```
rhf,wf,21,4,3;save,2130.2;
text,CASSCF, state averaged orbitals for 4SIG- states
multi,start,2130.2;orbital,2140.2;wf,21,4,3;state,3;maxiter,20;
ci,maxiter,30;wf,21,4,3;state,3;
---
```

5) The input file for the $^4\Sigma^+$ state

```
rhf,wf,21,1,3;save,2130.2;
text,CASSCF, state averaged orbitals for 4SIG+ states
multi,start,2130.2;orbital,2140.2;wf,21,1,3;state,2;maxiter,20;
ci,maxiter,30;wf,21,1,3;state,2;
---
```

6) The input file for the $^4\Pi$ state

```
rhf,wf,21,2,3;save,2130.2;
text,CASSCF, state averaged orbitals for 4PI states
multi,start,2130.2;orbital,2140.2;wf,21,2,3;state,2;wf,21,3,3;state,2;maxiter,20;
ci,wf,21,2,3;state,2;maxiter,30;
---
```

A.3.2 The input files for AsCl^+ with the ANO basis sets [32]

***, The MCSCF(CASSCF) calculation for the AsCl^+ excited states

```
memory,4,M
gprint,basis
file,2,ascl.wfu,new
zmat,angstrom
As
Cl,As,r
endz
```

basis={ Basis sets [32] and f functions given in the subsection 3.3.12.3}

```
r=1.988
```

```
int;
```

1) The input file for the $^2\Pi$ state

```
rhf,wf,49,2,1;save,2130.2;
text,CASSCF, state averaged orbitals for 2PI states
multi,start,2130.2;orbital,2140.2;wf,49,2,1;state,2;
wf,49,3,1;state,2;natorb,,ci,maxiter,20;
ci,maxiter,30;wf,49,2,1;state,2;
---
```

2) The input file for the $^2\Sigma^+$ state

```
rhf,wf,49,1,1;save,2130.2;  
text,CASSCF, state averaged orbitals for 2SIG+ states  
multi,start,2130.2;orbital,2140.2;wf,49,1,1;state,2;natorb,,ci;maxiter,20;  
ci;maxiter,30;wf,49,1,1;state,2;  
---
```

3) The input file for the $^2\Sigma^-$ state

```
rhf,wf,49,4,1;save,2130.2;  
text,CASSCF, state averaged orbitals for 2SIG- states  
multi,start,2130.2;orbital,2140.2;wf,49,4,1;state,4;natorb,,ci;maxiter,20;  
ci;maxiter,30;wf,49,4,1;state,4;  
---
```

4) The input file for the $^4\Sigma^-$ state

```
rhf,wf,49,4,3;save,2130.2;  
text,CASSCF, state averaged orbitals for 4SIG- states  
multi,start,2130.2;orbital,2140.2;wf,49,4,3;state,3;natorb,,ci;maxiter,20;  
ci;maxiter,30;wf,49,4,3;state,3;  
---
```

5) The input file for the $^4\Sigma^+$ state

```
rhf,wf,49,1,3;save,2130.2;  
text,CASSCF, state averaged orbitals for 4SIG+ states  
multi,start,2130.2;orbital,2140.2;wf,49,1,3;state,4;natorb,,ci;maxiter,20;  
ci;maxiter,30;wf,49,1,3;state,4;  
---
```

6) The input file for the $^4\Pi$ state

```
rhf,wf,49,2,3;save,2130.2;  
text,CASSCF, state averaged orbitals for 4PI states  
multi,start,2130.2;orbital,2140.2;wf,49,2,3;state,2;  
wf,49,3,3;state,2;natorb,,ci;maxiter,20;  
ci;wf,49,2,3;state,2;maxiter,30;  
---
```

A.4 The input files for BBr^+

As in the case of AsCl^+ , these consist of two categories, depending on the basis sets used.

A.4.1 The input files for BBr^+ with an effective core potential

***, The MCSCF(CASSCF) with ECP for the BBr^+ excited states

file,2,bbrplus.wfu,new


```

zmat,angstrom
br
b,br,r
endz
r=2.0
int;
ecp,1,ecp28mwb;
sp,1,ECP28mwb;c;
d,1,0.2;
spd,2,vqz(vdz or vtz);c

```

1) The input file for the $^2\Sigma^+$ state

```

rhf,wf,11,1,1;save,2130.2;
text,CASSCF, state averaged orbitals for 2SIG+ states
multi,start,2130.2;orbital,2140.2;wf,11,1,1;state,6;maxiter,25;
ci;maxiter,25;wf,11,1,1;state,6;
---
```

2) The input file for the $^2\Pi$ state

```

rhf,wf,11,2,1;save,2130.2;
text,CASSCF, state averaged orbitals for 2PI states
multi,start,2130.2;orbital,2140.2;wf,11,2,1;state,5;wf,11,3,1;state,5;maxiter,25;
ci;wf,11,2,1;state,5;maxiter,30;
---
```

3) The input file for the $^2\Sigma^-$ state

```

rhf,wf,11,4,1;save,2130.2;
text,CASSCF, state averaged orbitals for 2SIG- states
multi,start,2130.2;orbital,2140.2;wf,11,4,1;state,5;maxiter,25;
ci;wf,11,4,1;state,5;maxiter,30;
---
```

4) The input file for the $^4\Sigma^-$ state

```

rhf,wf,11,4,3;save,2130.2;
text,CASSCF, state averaged orbitals for 4SIG- states
multi,start,2130.2;orbital,2140.2;wf,11,4,3;state,5;maxiter,25;
ci;wf,11,4,3;state,5;maxiter,30;
---
```

5) The input file for the $^4\Sigma^+$ state

```
rhf,wf,11,1,3;save,2130.2;  
text,CASSCF, state averaged orbitals for 4SIG+ states  
multi;start,2130.2;orbital,2140.2;wf,11,1,3;state,5;maxiter,25;  
ci;wf,11,1,3;state,5;  
---
```

6) The input file for the $^4\Pi$ state

```
rhf,wf,11,2,3;save,2130.2;  
text,CASSCF, state averaged orbitals for 4PI states  
multi;start,2130.2;orbital,2140.2;wf,11,2,3;state,4;wf,11,3,3;state,4;maxiter,25;  
ci;wf,11,2,3;state,4;  
---
```

A.4.2 The input files for BBr^+ with the ANO basis sets [32]

*****, MCSCF(CASSCF) for BBr^+ excited states for all electron calculations**

```
memory,4,M  
gprint,basis  
file,2,bbr.wfu,new  
zmat,angstrom  
B  
Br,B,r  
endz
```

basis={Basis sets [32] and f functions introduced in the subsection 3.3.12.4}

r=2.5

int;

1) The input file for the $^2\Sigma^+$ state

```
rhf,wf,39,1,1;save,2130.2;  
text,CASSCF, state averaged orbitals for 2SIG+ states  
multi;start,2130.2;orbital,2140.2;wf,39,1,1;state,6;natorb,,ci;maxiter,25;  
ci;wf,39,1,1;state,6;maxiter,30;  
---
```

2) The input file for the $^2\Pi$ state

```
rhf,wf,39,2,1;save,2130.2;  
text,CASSCF, state averaged orbitals for 2PI states  
multi;start,2130.2;orbital,2140.2;wf,39,2,1;state,5;  
wf,39,3,1;state,5;natorb,,ci;maxiter,25;  
ci;wf,39,2,1;state,5;maxiter,30;  
---
```

3) The input file for the $^2\Sigma^-$ state

```
rhf,wf,39,4,1;save,2130.2;  
text,CASSCF, state averaged orbitals for 2SIG- states  
multi,start,2130.2;orbital,2140.2;wf,39,4,1;state,5;natorb,,ci;maxiter,25;  
ci,wf,39,4,1;state,5;maxiter,30;  
---
```

4) The input file for the $^4\Sigma^-$ state

```
rhf,wf,39,4,3;save,2130.2;  
text,CASSCF, state averaged orbitals for 4SIG- states  
multi,start,2130.2;orbital,2140.2;wf,39,4,3;state,5;natorb,,ci;maxiter,25;  
ci,wf,39,4,3;state,5;maxiter,30;  
---
```

5) The input file for the $^4\Sigma^+$ state

```
rhf,wf,39,1,3;save,2130.2;  
text,CASSCF, state averaged orbitals for 4SIG+ states  
multi,start,2130.2;orbital,2140.2;wf,39,1,3;state,5;natorb,,ci;maxiter,25;  
ci,wf,39,1,3;state,5;maxiter,30;  
---
```

6) The input file for the $^4\Pi$ state

```
rhf,wf,39,2,3;save,2130.2;  
text,CASSCF, state averaged orbitals for 4PI states  
multi,start,2130.2;orbital,2140.2;wf,39,2,3;state,4;  
wf,39,3,3;state,4;natorb,,ci;maxiter,25;  
ci,wf,39,2,3;state,4;maxiter,30;  
---
```


APPENDIX B

B.1 The results for NF^+ (VDZ and VTZ basis sets)

The CI results using the VDZ and VTZ basis sets are presented, in turn, in tables and figures **B.1.1** and **B.1.2** for the $^2\Pi$ state, **B.1.3** and **B.1.4** for the $^2\Sigma^+$ state, **B.1.5** and **B.1.6** for the $^2\Sigma^-$ state, **B.1.7** and **B.1.8** for the $^4\Sigma^-$ state, **B.1.9** and **B.1.10** for the $^4\Sigma^+$ state, and **B.1.11** and **B.1.12** for the $^4\Pi$ state.

B.2 The results for PCl^+ (VDZ and VTZ basis sets)

Tables and figures **B.2.1** to **B.2.12** (odd numbers mean the VDZ basis sets and even numbers mean the VTZ basis sets) for the CI results show that every pair of table and figure numbers correspond, in turn, to the $^2\Pi$, $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^-$, $^4\Sigma^+$ and $^4\Pi$ states respectively.

B.3 The results for AsCl^+ (VDZ, VTZ and VQZ basis sets) with ECP

The CI results with the VDZ, VTZ and VQZ basis sets are given, in turn, in tables and figures **B.3.1** to **B.3.3** for the $^2\Pi$ state, **B.3.4** to **B.3.6** for the $^2\Sigma^+$ state, **B.3.7** to **B.3.9** for the $^2\Sigma^-$ state, **B.3.10** to **B.3.12** for the $^4\Sigma^-$ state, **B.3.13** to **B.3.15** for the $^4\Sigma^+$ state, and **B.3.16** to **B.3.18** for the $^4\Pi$ state.

B.4 The results for BBr^+ (VDZ, VTZ and VQZ basis sets) with ECP

Tables and figures **B.4.1** to **B.4.3**, **B.4.4** to **B.4.6**, **B.4.7** to **B.4.9**, **B.4.10** to **B.4.12**, **B.4.13** to **B.4.15**, and **B.4.16** to **B.4.18** correspond to the $^2\Sigma^+$, $^2\Pi$, $^2\Sigma^-$, $^4\Sigma^-$, $^4\Sigma^+$ and $^4\Pi$ states, respectively for the CI results with, in turn, the VDZ, VTZ and VQZ basis sets.

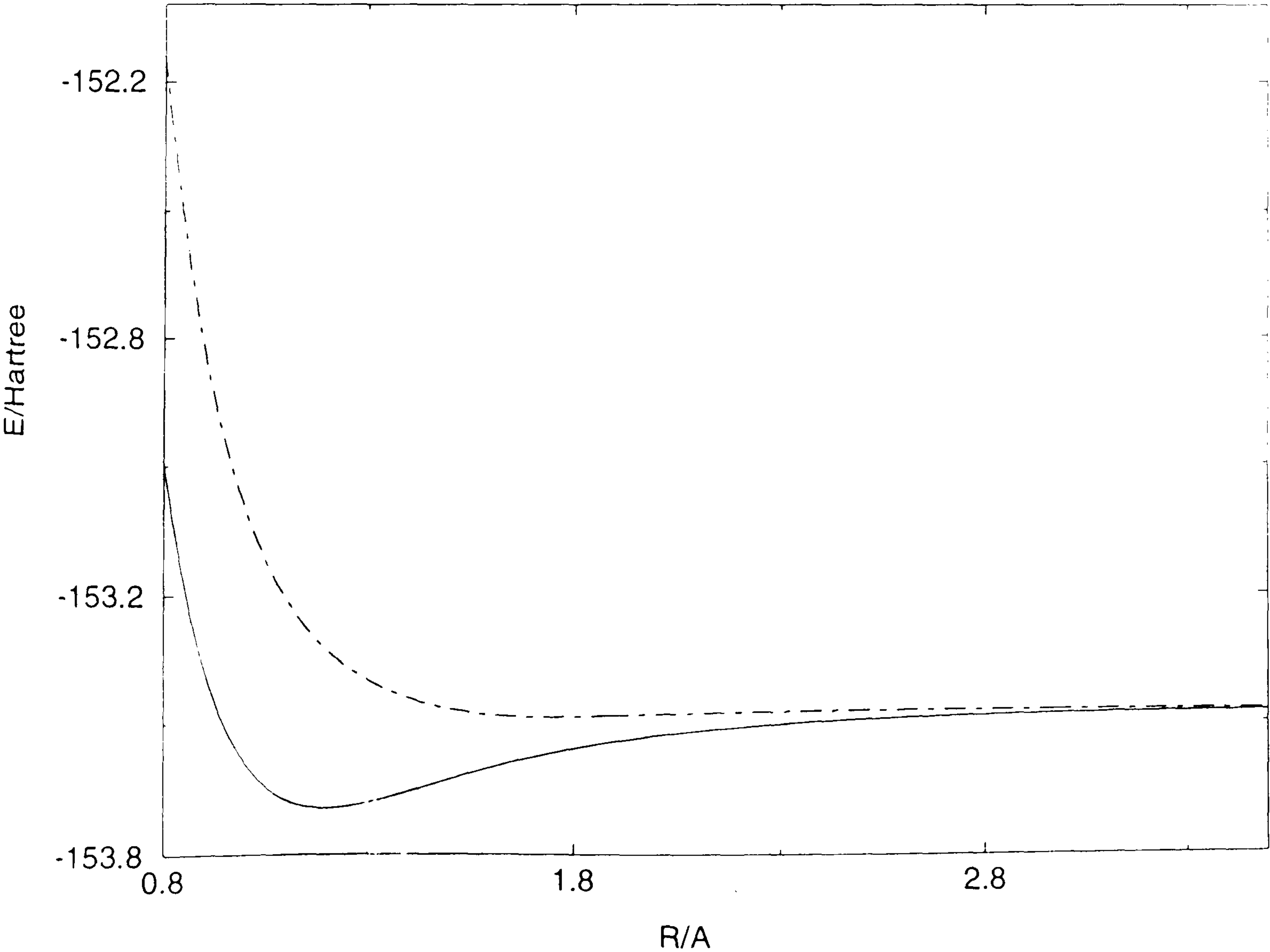
B.1.1 The CI results for the $^2\Pi$ states of NF^+ with the VDZ basis sets

Table B.1.1 Theoretical energy values

R/Å	ROOT1	ROOT2
0.8	-152.990219	-152.199786
0.9	-153.392964	-152.766188
1.0	-153.575498	-153.079722
1.1	-153.646103	-153.255169
1.2	-153.661136	-153.355448
1.3	-153.650370	-153.414383
1.4	-153.629292	-153.449660
1.5	-153.605636	-153.470274
1.6	-153.583132	-153.481083
1.7	-153.563454	-153.485212
1.8	-153.547191	-153.485345
1.9	-153.534158	-153.483766
2.0	-153.523701	-153.481838
2.1	-153.515158	-153.480101
2.2	-153.508067	-153.478667
2.3	-153.502143	-153.477509
2.4	-153.497202	-153.476586
2.5	-153.493107	-153.475865
2.75	-153.485842	-153.474764
3.0	-153.481624	-153.474357
3.5	-153.477991	-153.474416

E/Hartree

Figure B.1.1 Calculated potential energy curves



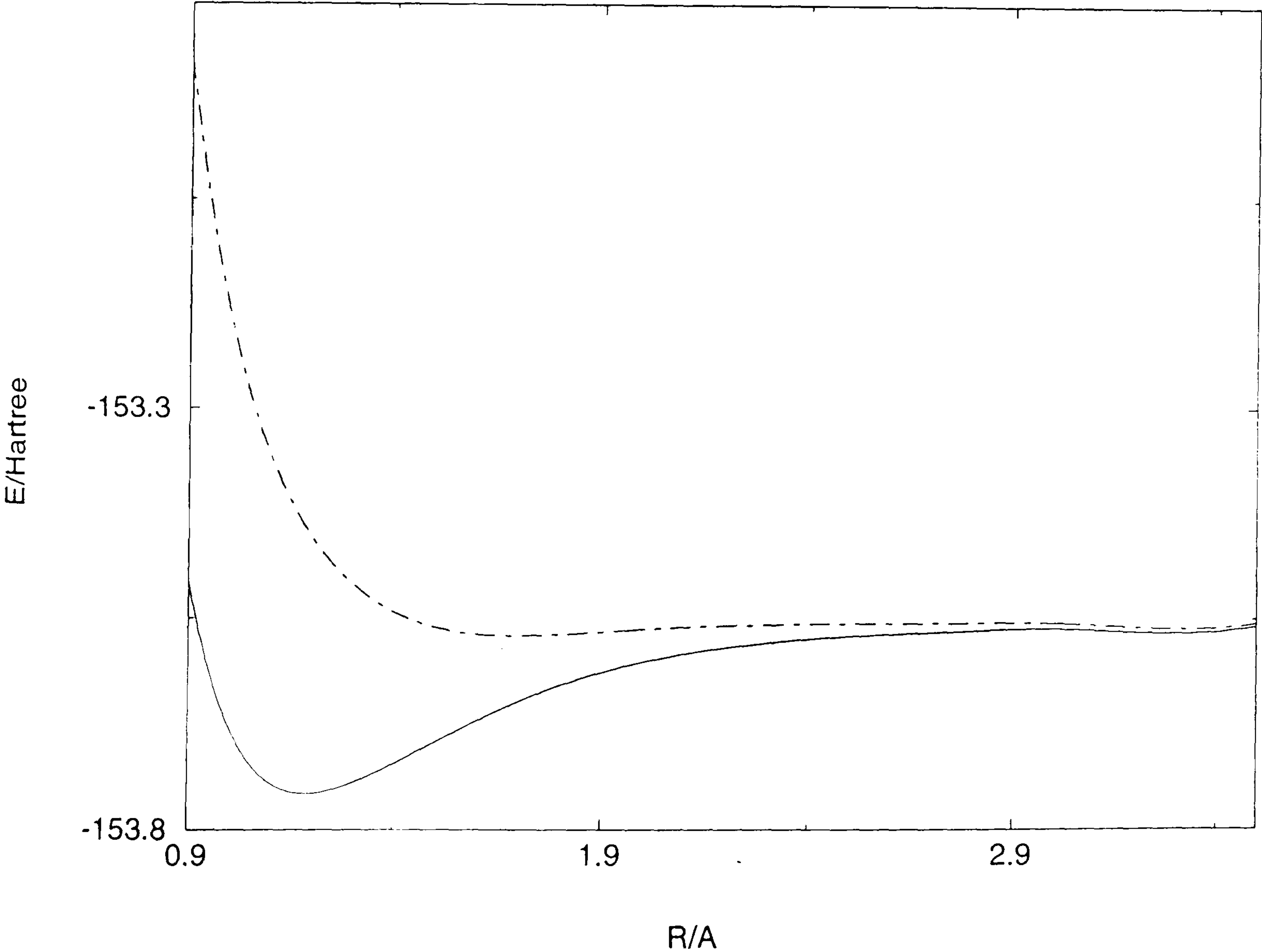
B.1.2 The CI results for the $^2\Pi$ states of NF^+ with the VTZ basis sets

Table B.1.2 Theoretical energy values

R/Å	ROOT1	ROOT2
0.85	-153.381957	-152.683325
0.90	-153.536912	-152.915012
1.00	-153.709156	-153.216868
1.10	-153.775108	-153.386595
1.20	-153.788092	-153.483881
1.30	-153.775980	-153.540644
1.40	-153.753217	-153.573653
1.50	-153.727285	-153.591775
1.75	-153.669552	-153.601399
2.00	-153.633104	-153.594568
2.25	-153.613282	-153.589730
2.50	-153.602651	-153.587601
2.75	-153.596864	-153.586806
3.00	-153.593612	-153.586598
3.50	-153.590540	-153.586762

E/Hartree

Figure B.1.2 Calculated potential energy curves



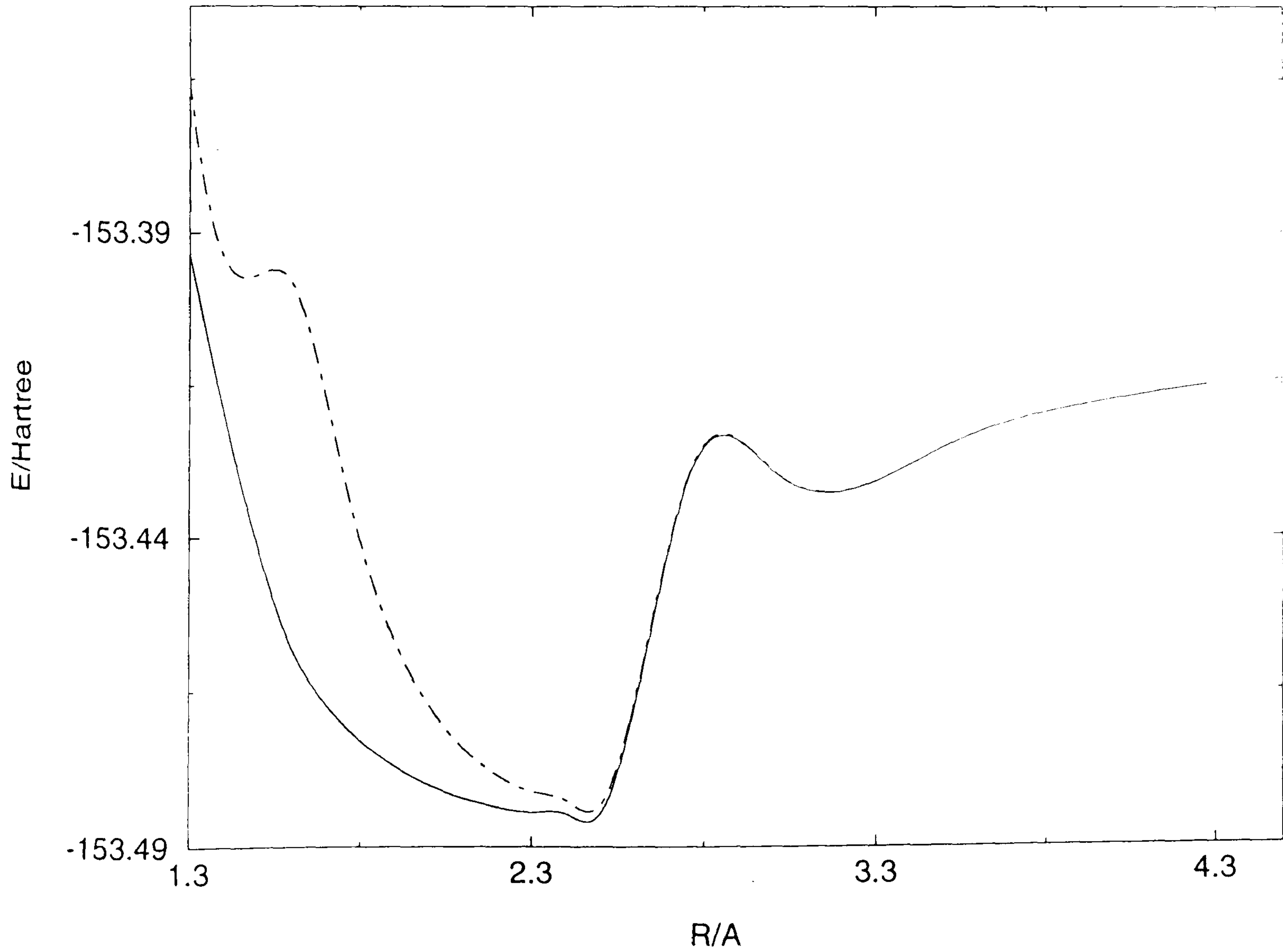
B.1.3 The CI results for the $^2\Sigma^+$ states of NF^+ with the VDZ basis sets

Table B.1.3 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-153.390067	-153.361872
1.5	-153.437909	-153.393915
1.6	-153.454498	-153.394844
1.7	-153.463849	-153.413826
1.8	-153.469754	-153.437406
1.9	-153.473923	-153.453370
2.0	-153.477024	-153.464040
2.1	-153.479243	-153.471023
2.2	-153.480687	-153.475453
2.3	-153.481486	-153.478126
2.4	-153.481782	-153.479603
2.5	-153.481698	-153.480270
2.75	-153.427623	-153.427112
3.0	-153.426238	-153.426020
3.5	-153.422208	-153.422143
4.0	-153.414484	-153.414454
4.5	-153.411251	-153.411235

E/Hartree

Figure B.1.3 Calculated potential energy curves



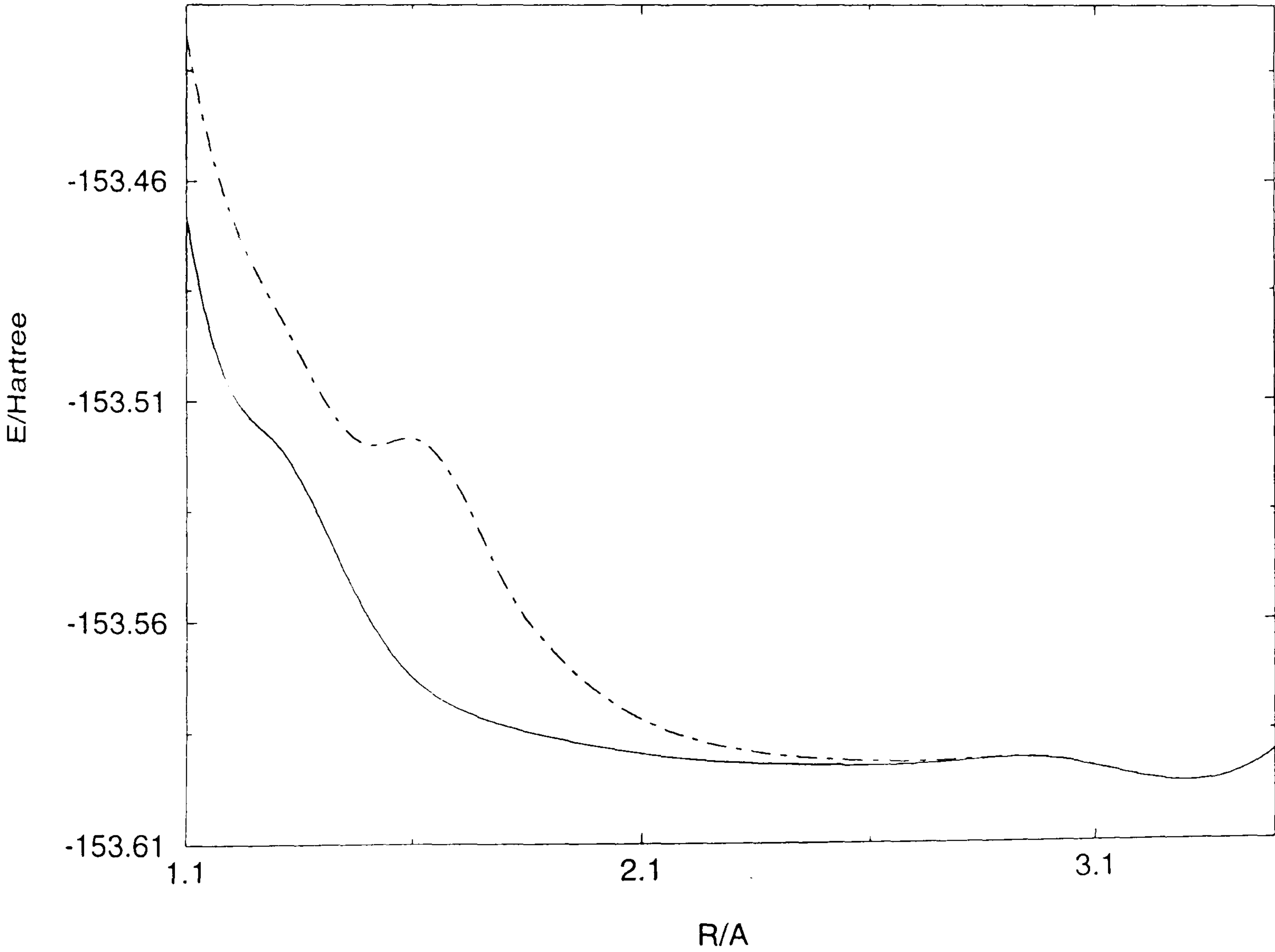
B.1.4 The CI results for the $^2\Sigma^+$ states of NF^+ with the VTZ basis sets

B.1.4 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.1	-153.467664	-153.427212	-153.282342	-153.144669	-153.108931
1.2	-153.507677	-153.467861	-153.396784	-153.232014	-153.201014
1.3	-153.519550	-153.489095	-153.469305	-153.290126	-153.260029
1.5	-153.558363	-153.519808	-153.476491	-153.448253	-153.419701
1.6	-153.572353	-153.518485	-153.496475	-153.477639	-153.462681
1.7	-153.579433	-153.529692	-153.516568	-153.492343	-153.478072
1.8	-153.583360	-153.551426	-153.515698	-153.508065	-153.494330
1.9	-153.586028	-153.565975	-153.516622	-153.515366	-153.505071
2.0	-153.588166	-153.575674	-153.520712	-153.516022	-153.510540
2.25	-153.591652	-153.587717	-153.522698	-153.520087	-153.512475
2.5	-153.592710	-153.591362	-153.521745	-153.520831	-153.512587
2.75	-153.592406	-153.591891	-153.520484	-153.520140	-153.512776
3.0	-153.591626	-153.591401	-153.519307	-153.519159	-153.513031
3.5	-153.590118	-153.590044	-153.517530	-153.517466	-153.514041

E/Hartree

Figure B.1.4 Calculated potential energy curves



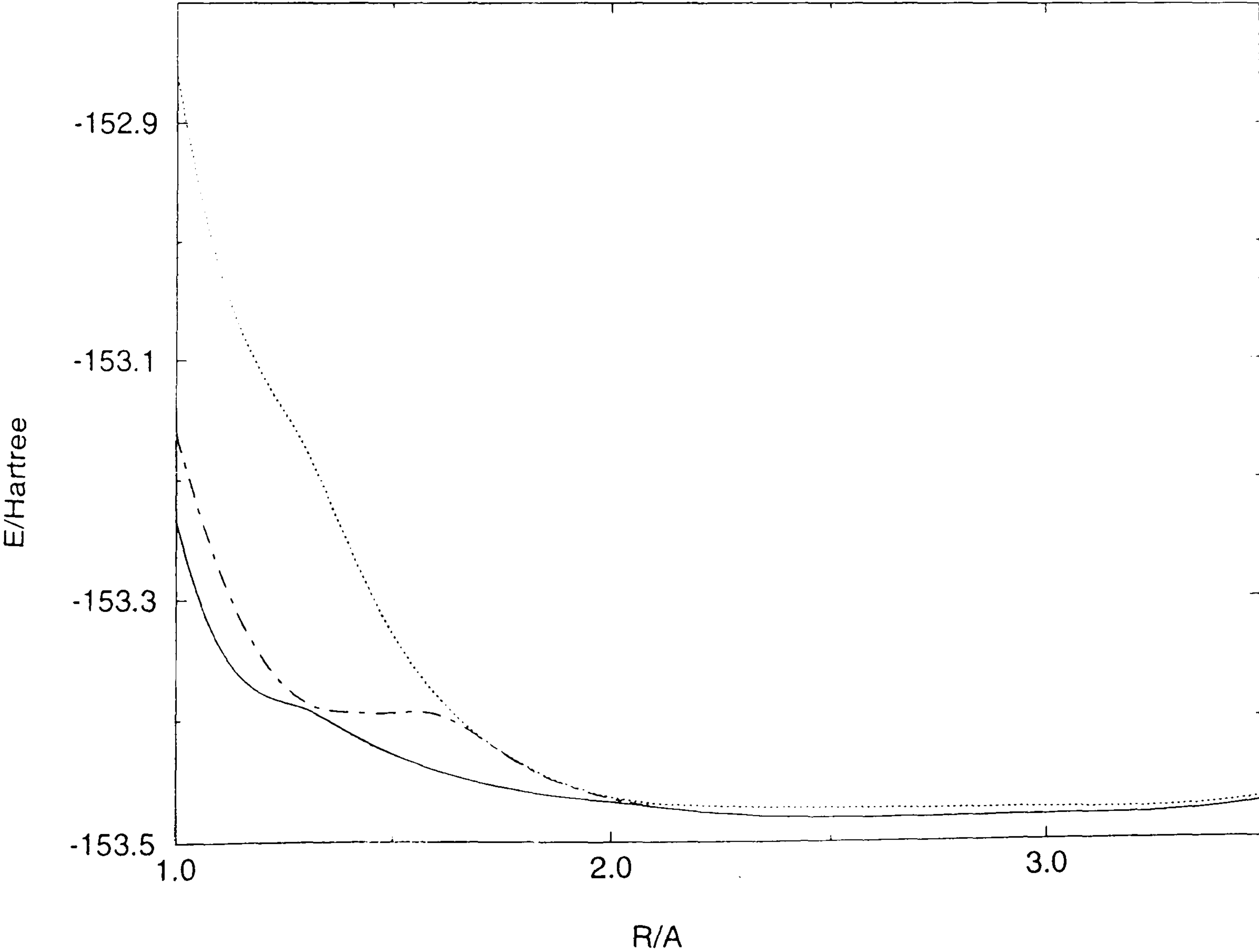
B.1.5 The CI results for the $^2\Sigma^-$ states of NF^+ with the VDZ basis sets

Table B.1.5 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.0	-153.232262	-153.159364	-152.855639
1.2	-153.377206	-153.346687	-153.110689
1.3	-153.390258	-153.384650	-153.173016
1.4	-153.409795	-153.392976	-153.253651
1.5	-153.427764	-153.393731	-153.327368
1.6	-153.440955	-153.394515	-153.378333
1.7	-153.450614	-153.413691	-153.412838
1.8	-153.457836	-153.437320	-153.436454
1.9	-153.463092	-153.453313	-153.452411
2.0	-153.467012	-153.463998	-153.462859
2.1	-153.471161	-153.470990	-153.468227
2.2	-153.475424	-153.475234	-153.470275
2.3	-153.478101	-153.477868	-153.471425
2.4	-153.479587	-153.479363	-153.472136
2.5	-153.480278	-153.480076	-153.472586
2.75	-153.480169	-153.480027	-153.473171
3.0	-153.479160	-153.479062	-153.473498
3.5	-153.469822	-153.469773	-153.466378

E/Hartree

Figure B.1.5 Calculated potential energy curves



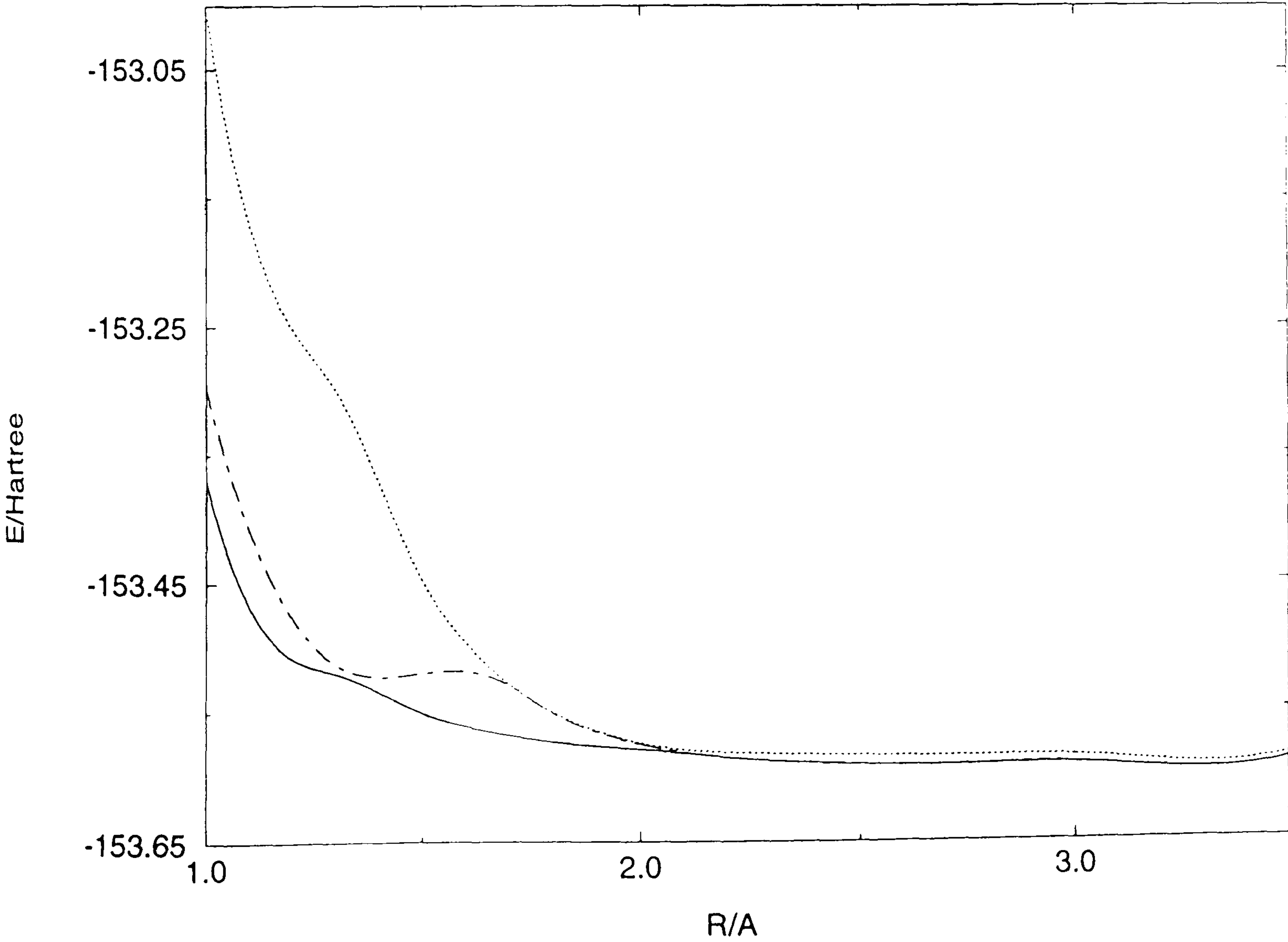
B.1.6 The CI results for the $^2\Sigma^-$ states of NF^+ with the VTZ basis sets

Table B.1.6 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.00	-153.369138	-153.297334	-153.000334
1.20	-153.507927	-153.476560	-153.251633
1.30	-153.519481	-153.512189	-153.299172
1.50	-153.550200	-153.519195	-153.447160
1.60	-153.560740	-153.517775	-153.495863
1.70	-153.567841	-153.529022	-153.528179
1.80	-153.573058	-153.550949	-153.550083
1.90	-153.576778	-153.565654	-153.564766
2.00	-153.579565	-153.575465	-153.574441
2.10	-153.582469	-153.581951	-153.579938
2.20	-153.586170	-153.586041	-153.581980
2.30	-153.588841	-153.588630	-153.583087
2.40	-153.590458	-153.590247	-153.583845
2.50	-153.591365	-153.591172	-153.584393
2.75	-153.591914	-153.591776	-153.585247
3.00	-153.591429	-153.591335	-153.585750
3.50	-153.589903	-153.589858	-153.586226

E/Hartree

Figure B.1.6 Calculated potential energy curves



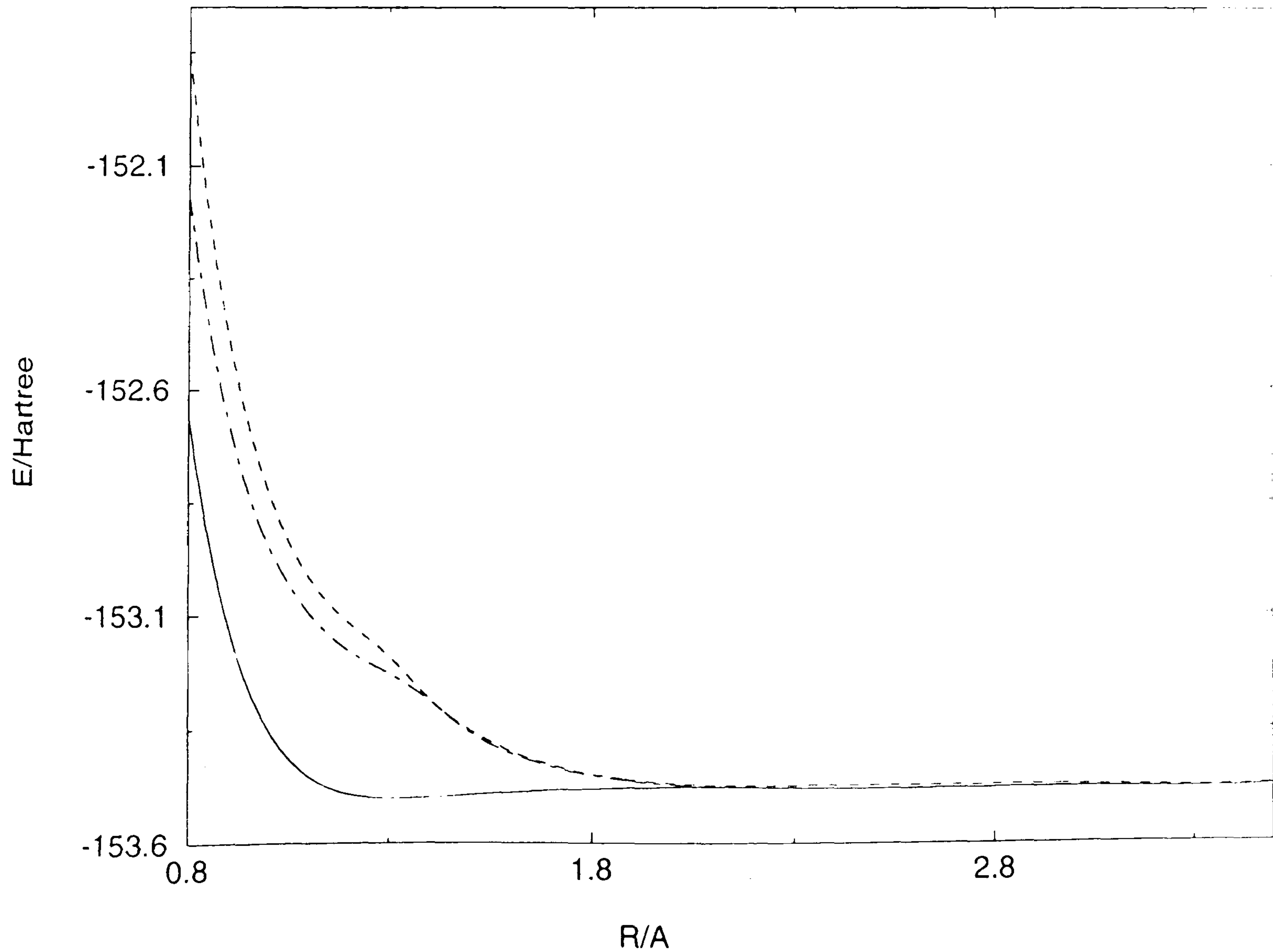
B.1.7 The CI results for the $^4\Sigma^-$ states of NF^+ with the VDZ basis sets

Table B.1.7 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
0.8	-152.657441	-152.163608	-151.851131
0.9	-153.123468	-152.669644	-152.475898
1.0	-153.351141	-152.941917	-152.822446
1.1	-153.453922	-153.091623	-153.012073
1.2	-153.493249	-153.176008	-153.114006
1.3	-153.502776	-153.226318	-153.188230
1.4	-153.500832	-153.287096	-153.284327
1.5	-153.495388	-153.356023	-153.351007
1.6	-153.489825	-153.401876	-153.397375
1.7	-153.485365	-153.432062	-153.428286
1.8	-153.482199	-153.451750	-153.448600
1.9	-153.480133	-153.464438	-153.461718
2.0	-153.478975	-153.472451	-153.469827
2.1	-153.478963	-153.477337	-153.473988
2.2	-153.480233	-153.480142	-153.474965
2.3	-153.481575	-153.481369	-153.474817
2.4	-153.482121	-153.481873	-153.474502
2.5	-153.482110	-153.481880	-153.474210
2.75	-153.480953	-153.480797	-153.473778
3.0	-153.479477	-153.479375	-153.473713
3.5	-153.477558	-153.477510	-153.474099

E/Hartree

Figure B.1.7 Calculated potential energy curves



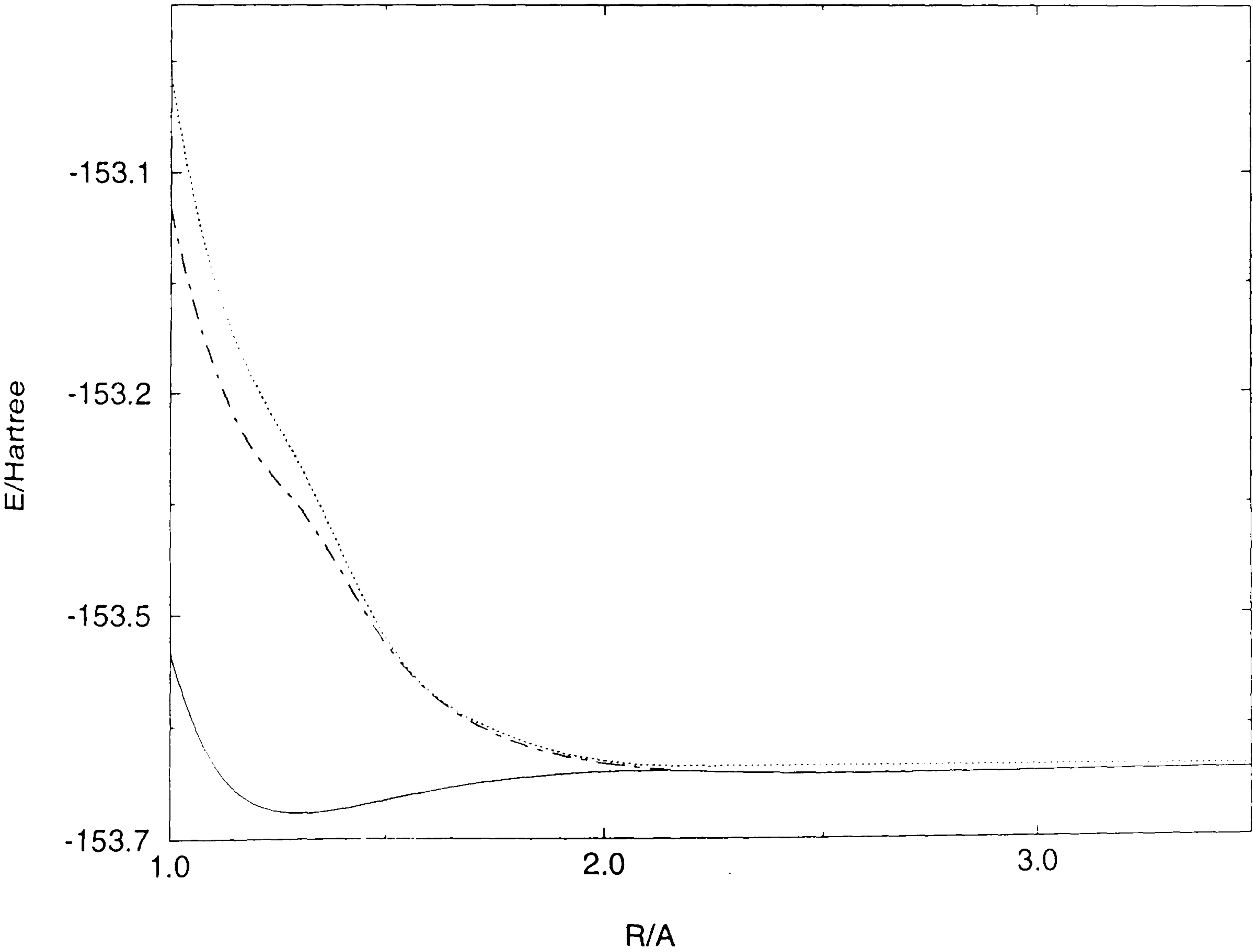
B.1.8 The CI results for the $^4\Sigma^-$ states of NF^+ with the VTZ basis sets

Table B.1.8 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.00	-153.483097	-153.081406	-152.959281
1.10	-153.581330	-153.223850	-153.143520
1.20	-153.618573	-153.304200	-153.242624
1.30	-153.626689	-153.351895	-153.312696
1.50	-153.615276	-153.475002	-153.469918
1.75	-153.598396	-153.556585	-153.553170
1.90	-153.592838	-153.576017	-153.573398
2.00	-153.590761	-153.583222	-153.580802
2.10	-153.589963	-153.587688	-153.584874
2.20	-153.590667	-153.590372	-153.586120
2.30	-153.591895	-153.591758	-153.586114
2.40	-153.592662	-153.592447	-153.585948
2.50	-153.592946	-153.592734	-153.585827
2.75	-153.592586	-153.592436	-153.585775
3.00	-153.591701	-153.591602	-153.585929
3.50	-153.590115	-153.590070	-153.586413

E/Hartree

Figure B.1.8 Calculated potential energy curves



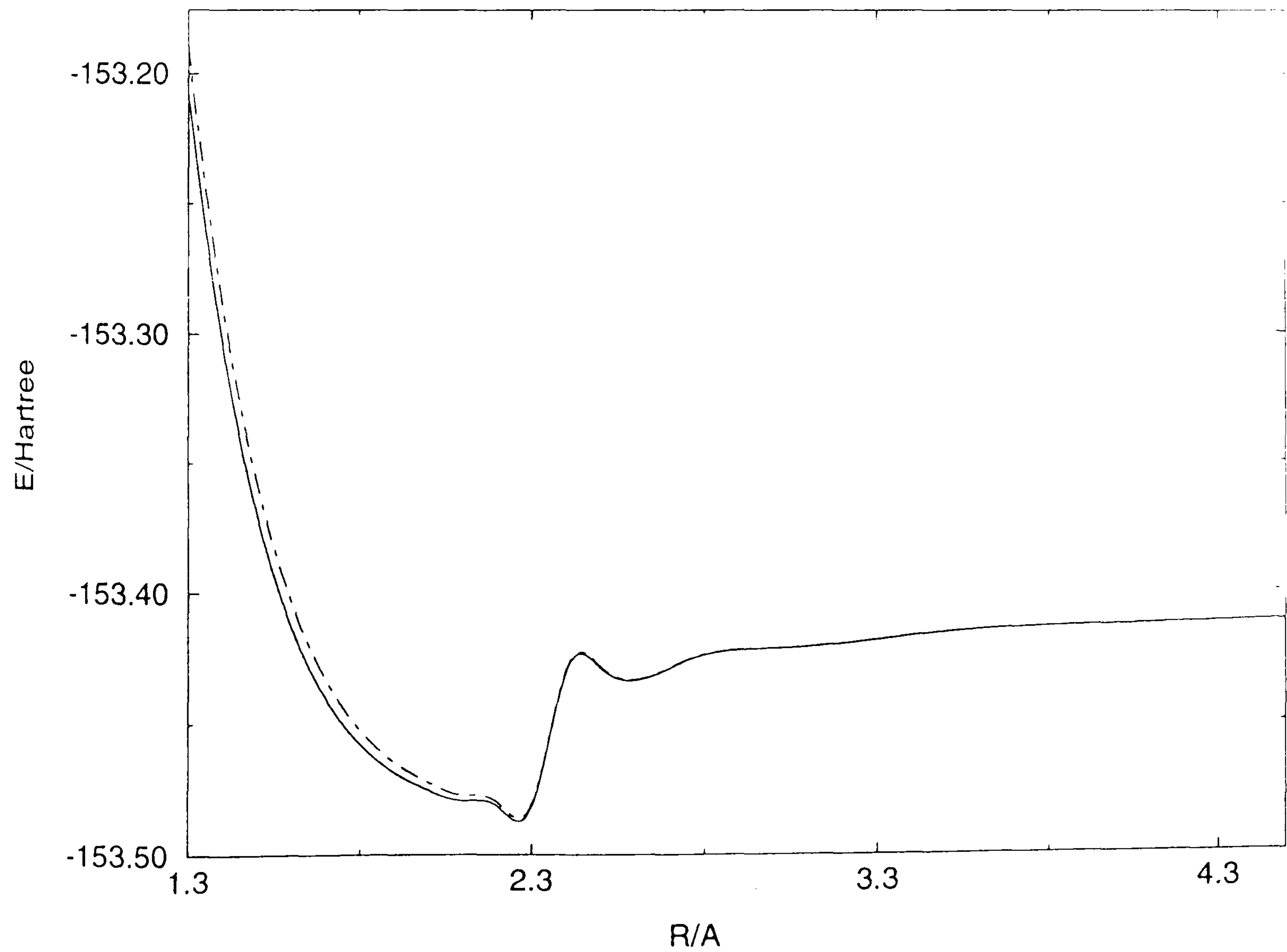
B.1.9 The CI results for the $^4\Sigma^+$ states of NF^+ with the VDZ basis sets

Table B.1.9 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-153.205468	-153.188770
1.5	-153.368673	-153.356232
1.6	-153.411715	-153.401993
1.7	-153.439540	-153.432094
1.8	-153.457302	-153.451716
1.9	-153.468465	-153.464352
2.0	-153.475290	-153.472305
2.1	-153.479241	-153.477094
2.2	-153.481265	-153.479729
2.3	-153.481673	-153.480572
2.4	-153.429424	-153.428653
2.5	-153.428974	-153.428410
2.75	-153.425856	-153.425579
3.0	-153.421630	-153.421479
3.5	-153.415527	-153.415468
4.0	-153.412617	-153.412588
4.5	-153.411078	-153.411062

E/Hartree

Figure B.1.9 Calculated potential energy values



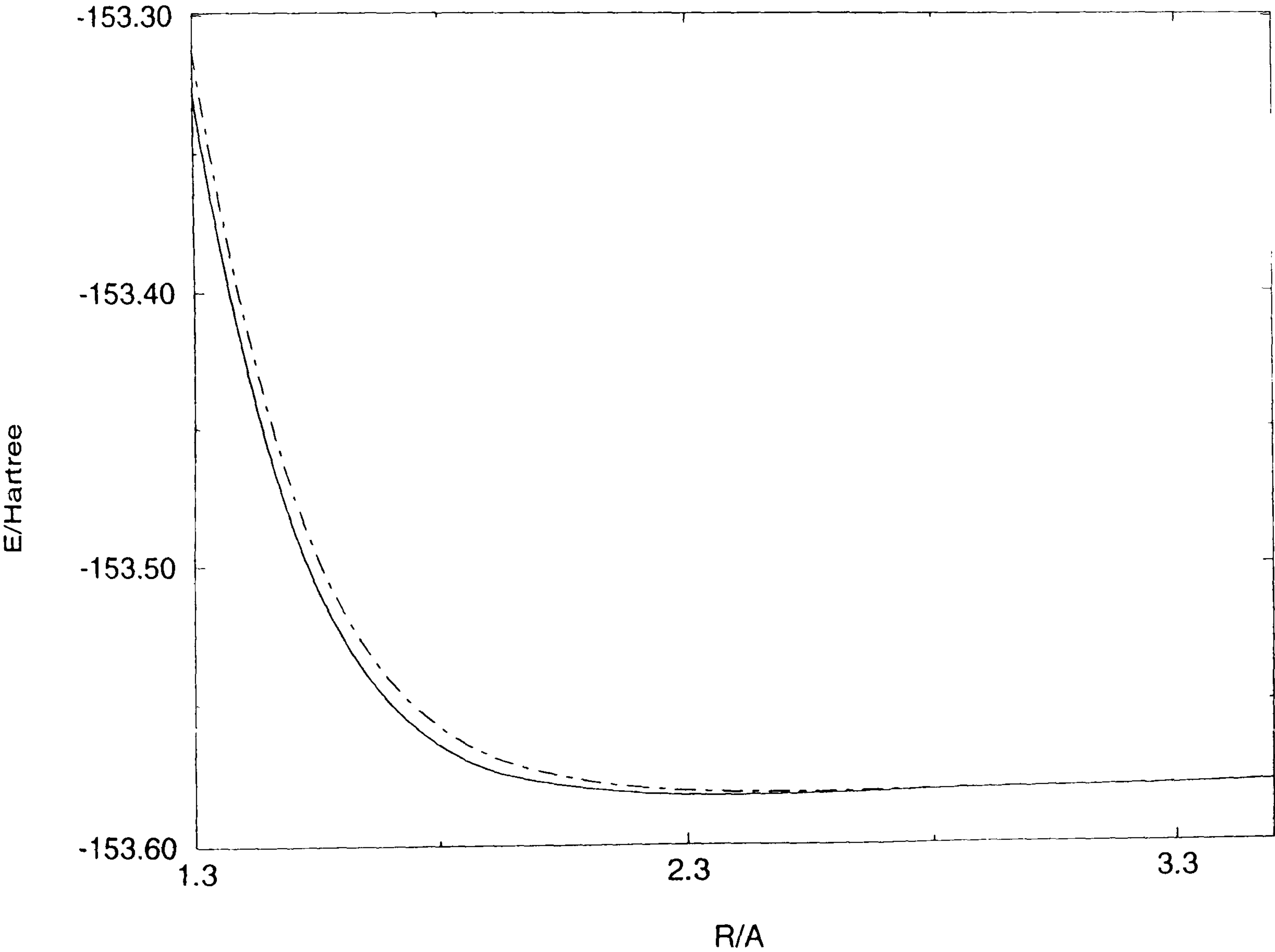
B.1.10 The results for the $^4\Sigma^+$ states of NF^+ with the VTZ basis sets

Table B.1.10 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.3	-153.329433	-153.313448	-153.285531	-153.284741	-152.952708
1.5	-153.485602	-153.472953	-153.329936	-153.327418	-153.224877
1.6	-153.525541	-153.515321	-153.337601	-153.335867	-153.305035
1.7	-153.550375	-153.542176	-153.362829	-153.343819	-153.341243
1.8	-153.565424	-153.558910	-153.402071	-153.350219	-153.348147
1.9	-153.574237	-153.569136	-153.429672	-153.357214	-153.355071
2.0	-153.578496	-153.574750	-153.449239	-153.366017	-153.359641
2.25	-153.583178	-153.581464	-153.474364	-153.380719	-153.383133
2.5	-153.583399	-153.582648	-153.483018	-153.389497	-153.387432
2.75	-153.582328	-153.581993	-153.485441	-153.391123	-153.389118
3.0	-153.581579	-153.581417	-153.486159	-153.391644	-153.389574
3.5	-153.579655	-153.579586	-153.485320	-153.390826	-153.388602

E/Hartree

Figure B.1.10 Calculated potential energy curves



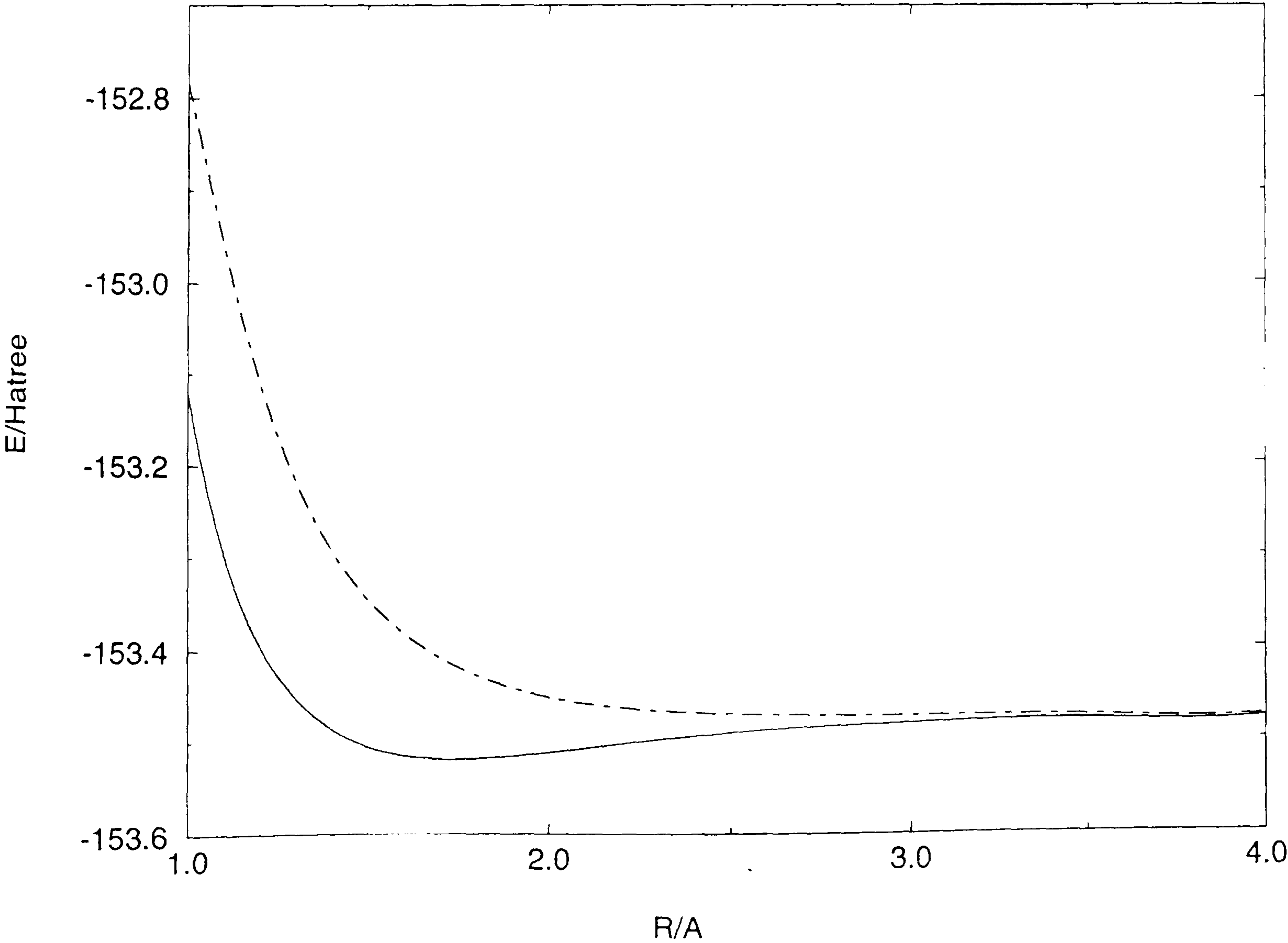
B.1.11 The CI results for the $^4\Pi$ states of NF^+ with the VDZ basis sets

Table B.1.11 Theoretical energy values

R/Å	ROOT1	ROOT2
1.0	-153.117798	-152.781403
1.1	-153.294224	-152.955980
1.2	-153.394289	-153.105400
1.3	-153.452247	-153.215242
1.4	-153.486147	-153.291532
1.5	-153.505331	-153.344444
1.6	-153.514951	-153.381694
1.7	-153.518355	-153.408248
1.8	-153.517904	-153.427449
1.9	-153.515183	-153.441375
2.0	-153.511257	-153.451369
2.1	-153.506846	-153.458438
2.2	-153.502416	-153.463371
2.3	-153.498246	-153.466776
2.4	-153.494488	-153.469103
2.5	-153.491203	-153.470681
2.75	-153.485035	-153.472734
3.0	-153.481260	-153.473555
3.5	-153.477904	-153.474276
4.0	-153.476923	-153.474738

E/Hartree

Figure B.1.11 Calculated potential energy curves



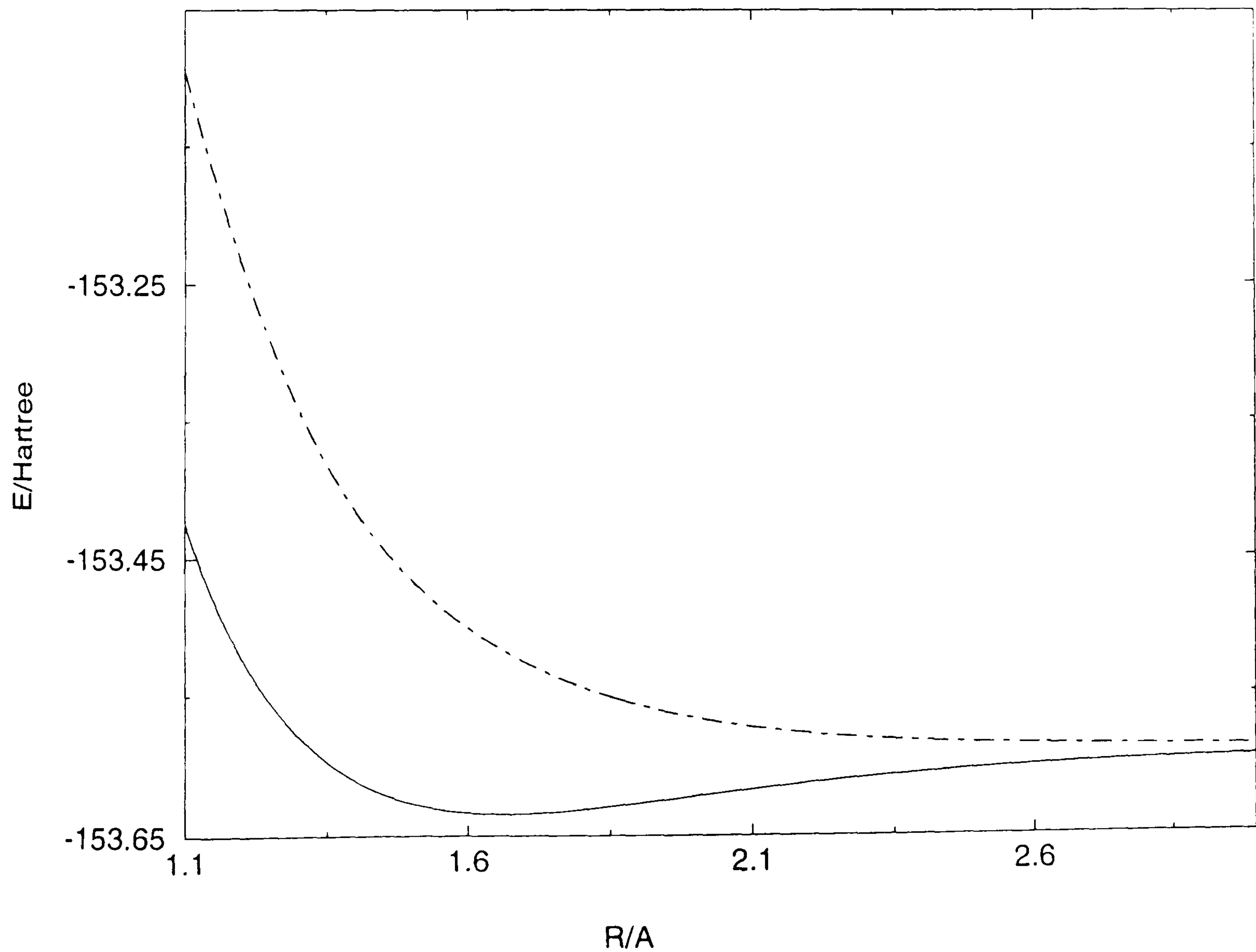
B.1.12 The CI results for the $^4\Pi$ states of NF^+ with the VTZ basis sets

Table B.1.12 Theoretical energy values

R/Å	ROOT1	ROOT2
1.10	-153.423121	-153.094183
1.20	-153.520452	-153.232361
1.30	-153.576315	-153.338057
1.50	-153.624575	-153.462516
1.60	-153.631437	-153.498244
1.70	-153.632213	-153.523549
1.80	-153.629543	-153.541717
1.90	-153.625154	-153.554819
2.00	-153.620167	-153.564199
2.10	-153.615269	-153.570858
2.20	-153.610823	-153.575551
2.30	-153.606971	-153.578840
2.40	-153.603722	-153.581136
2.50	-153.601028	-153.582735
2.75	-153.596232	-153.584930
3.00	-153.593338	-153.585876

E/Hartree

Figure B.1.12 Calculated potential energy curves



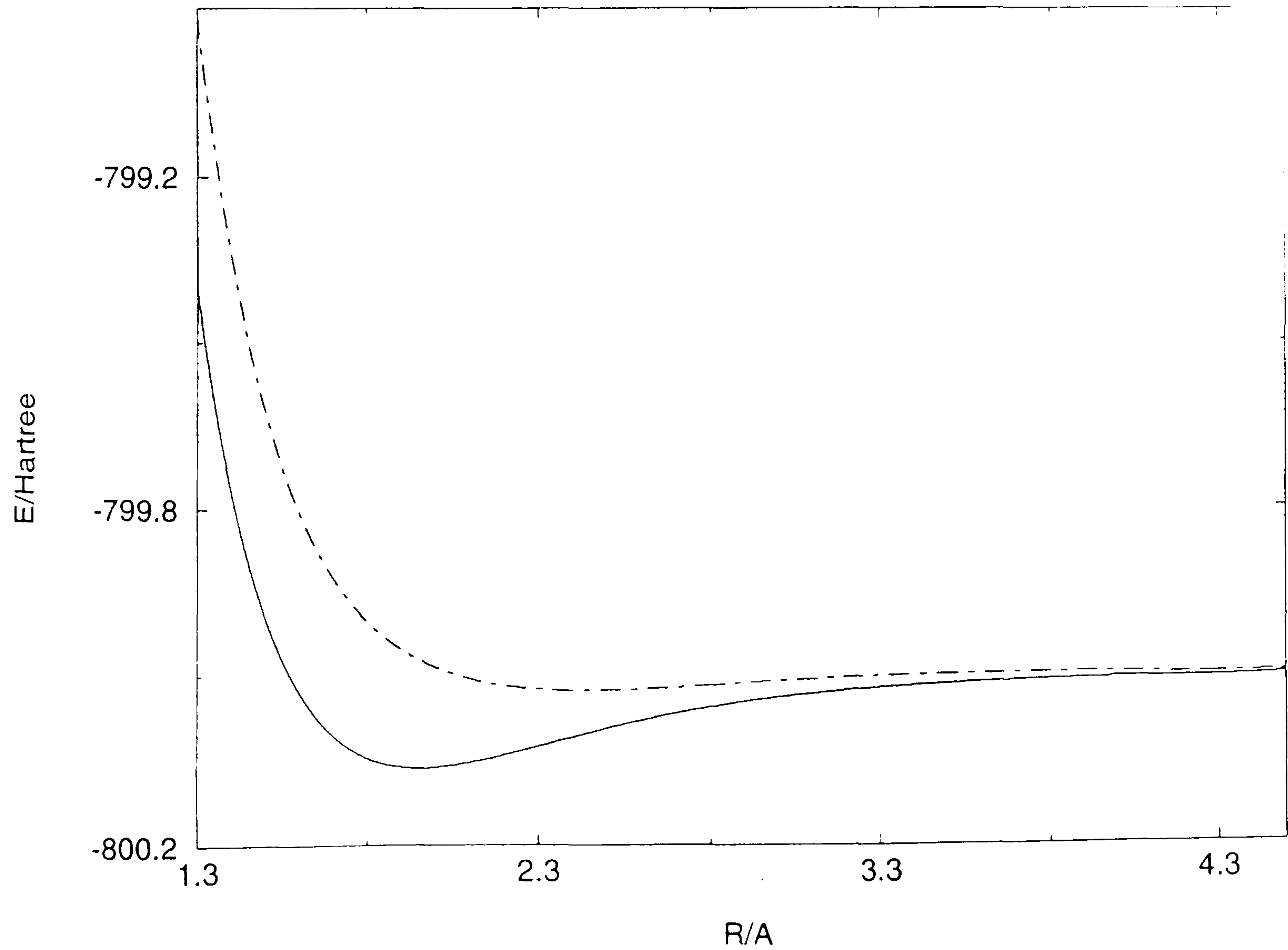
B.2.1 The CI results for the $^2\Pi$ states of PCI^+ with the VDZ basis sets

Table B.2.1 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-799.418590	-799.012598
1.5	-799.910249	-799.596181
1.6	-800.024206	-799.749662
1.7	-800.089144	-799.850711
1.8	-800.122370	-799.916801
1.9	-800.135416	-799.959719
2.0	-800.135900	-799.987210
2.1	-800.128868	-800.004375
2.2	-800.117671	-800.014567
2.25	-800.111241	-800.017774
2.3	-800.104546	-800.020004
2.4	-800.090989	-800.022168
2.5	-800.077986	-800.022080
2.75	-800.051187	-800.016489
3.0	-800.033466	-800.009122
3.5	-800.014607	-800.000921
4.0	-800.006387	-799.998697
4.5	-800.002671	-799.998036
5.0	-799.960843	-799.957373

E/Hartree

Figure B.2.1 Calculated potential energy curves



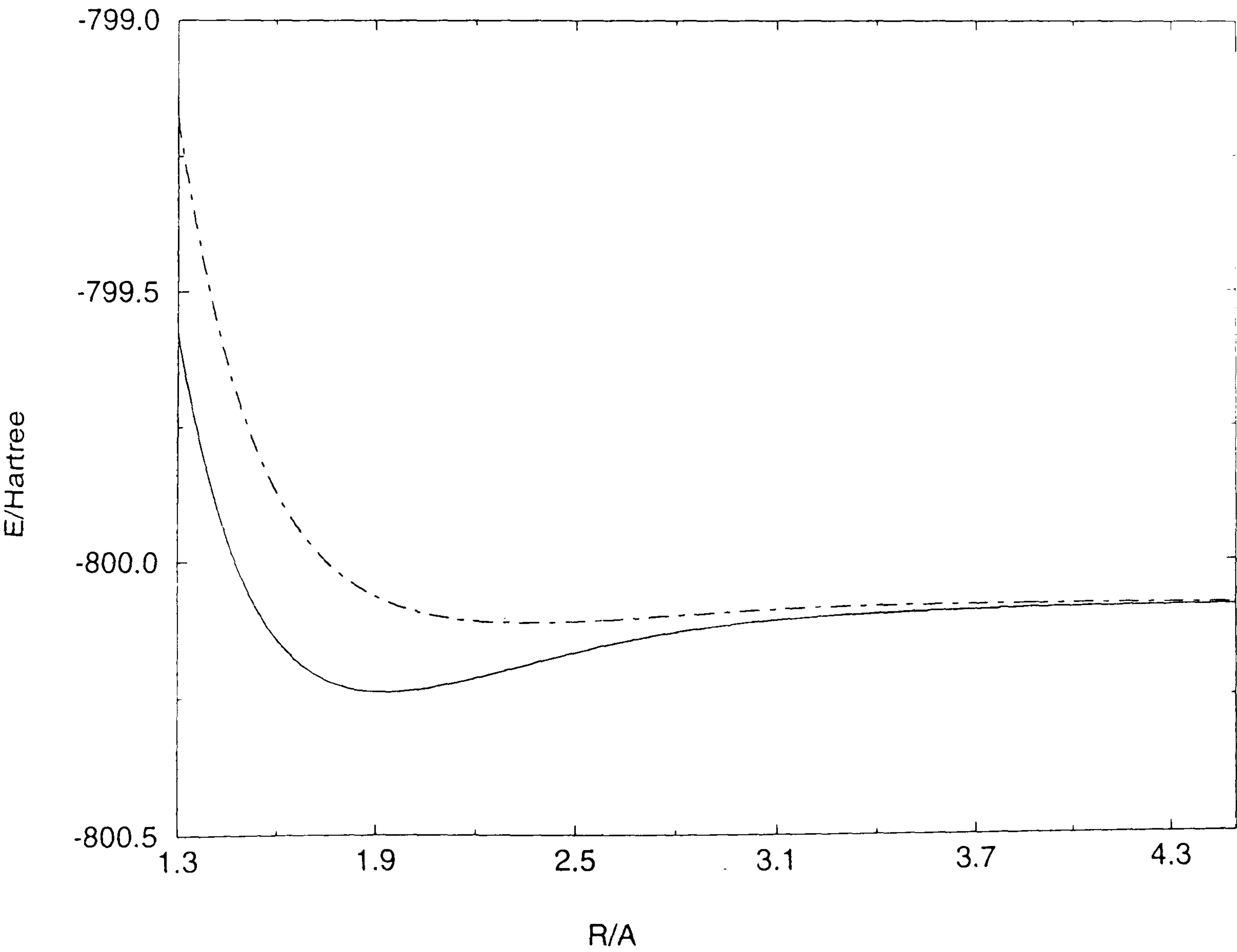
B.2.2 The CI results for the $^2\Pi$ states of PCl^+ with the VTZ basis sets

Table B.2.2 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-799.575262	-799.178854
1.5	-800.036023	-799.728414
1.6	-800.140147	-799.870723
1.7	-800.198205	-799.963327
1.8	-800.226736	-800.023429
1.9	-800.236424	-800.061963
2.0	-800.234418	-800.086113
2.1	-800.225399	-800.100642
2.2	-800.212467	-800.108685
2.3	-800.197695	-800.112322
2.4	-800.182484	-800.112950
2.5	-800.167782	-800.111537
2.75	-800.136802	-800.103284
3.0	-800.116095	-800.093761
3.5	-800.095714	-800.083225
4.0	-800.087765	-800.080500
4.5	-800.084079	-800.079560

E/Hartree

Figure B.2.2 Calculated potential energy curves



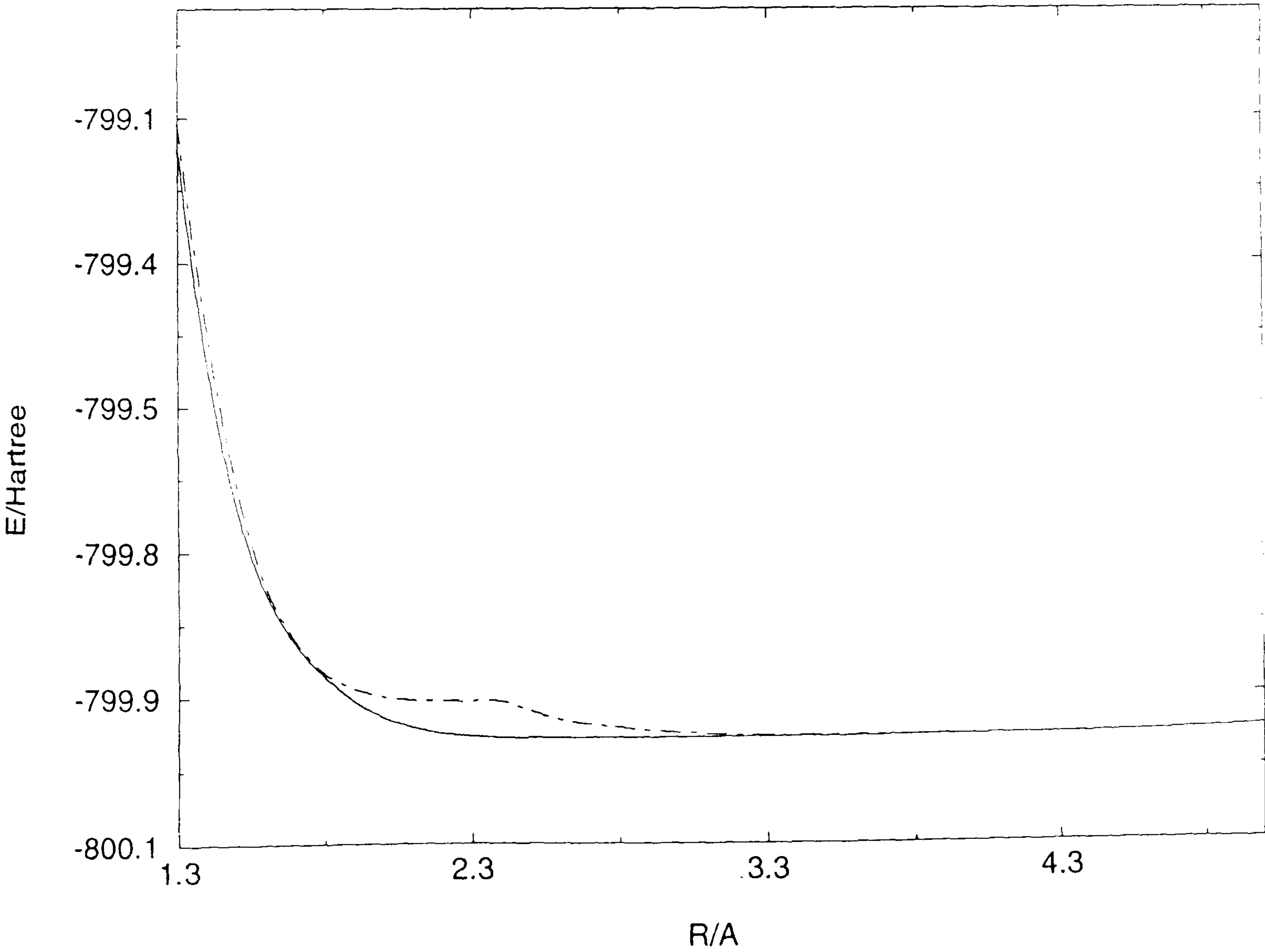
B.2.3 The CI results for the $^2\Sigma^+$ states of PCl^+ with the VDZ basis sets

Table B.2.3 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-799.188086	-799.156502
1.5	-799.687895	-799.657954
1.6	-799.805730	-799.795925
1.7	-799.876100	-799.871190
1.8	-799.920768	-799.915898
1.9	-799.954418	-799.937124
2.0	-799.976607	-799.947635
2.1	-799.990492	-799.952351
2.2	-799.998577	-799.954158
2.25	-800.001067	-799.954490
2.3	-800.002791	-799.954604
2.4	-800.004796	-799.955503
2.5	-800.005258	-799.969071
2.75	-800.005050	-799.989554
3.0	-800.005301	-799.998901
3.5	-800.005105	-800.003848
4.0	-800.003620	-800.003282
4.5	-800.002020	-800.001888
5.0	-799.995160	-799.995092

E/Hartree

Figure B.2.3 Calculated potential energy curves



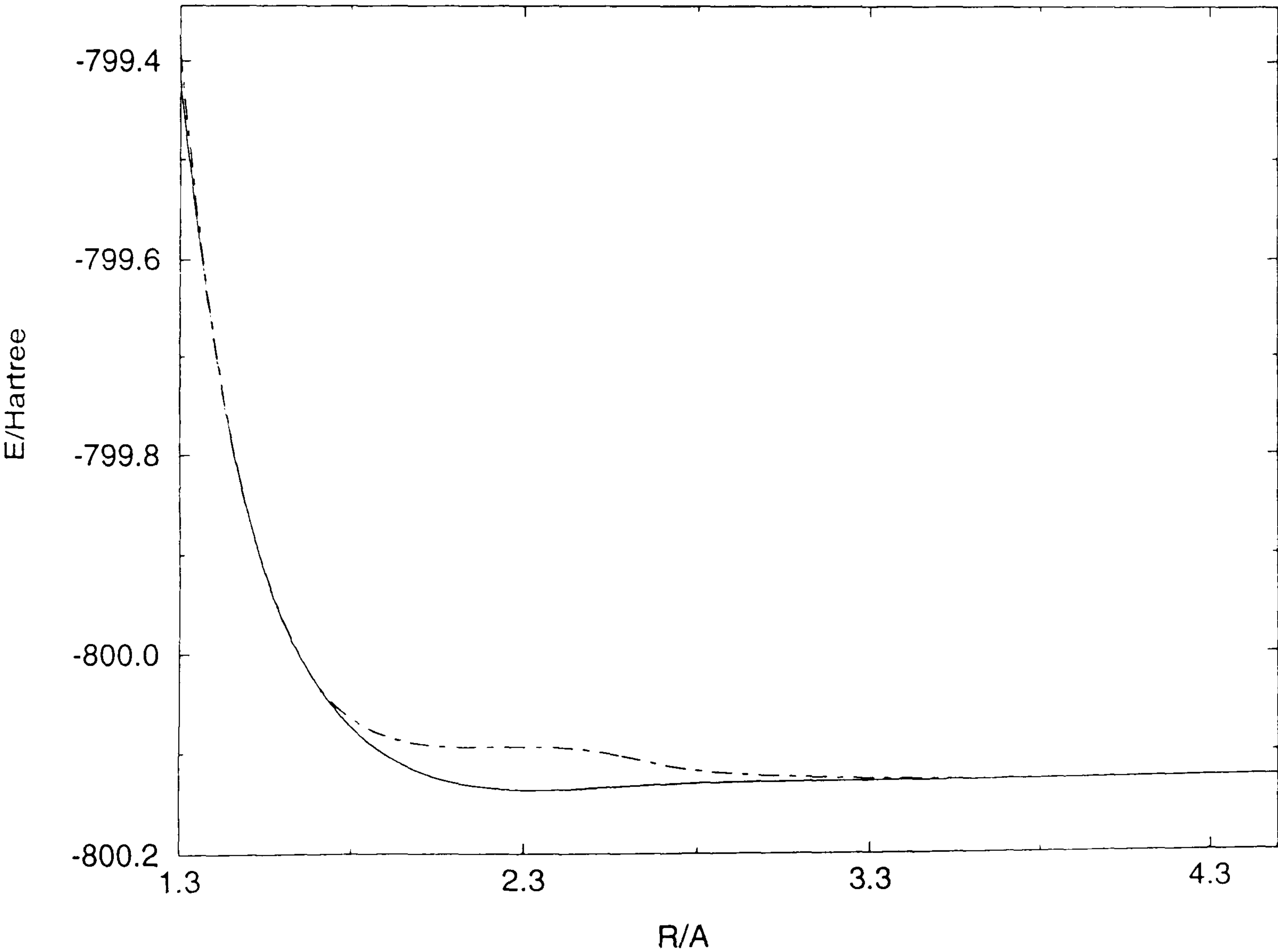
B.2.4 The CI results for the $^2\Sigma^+$ states of PCl^+ with the VTZ basis sets

Table B.2.4 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-799.376437	-799.348083
1.5	-799.816539	-799.815473
1.6	-799.924357	-799.922221
1.7	-799.988676	-799.987754
1.8	-800.031413	-800.022786
1.9	-800.059586	-800.040814
2.0	-800.077517	-800.049146
2.1	-800.088027	-800.052270
2.2	-800.093341	-800.052764
2.5	-800.093838	-800.056842
2.75	-800.089978	-800.074496
3.0	-800.088225	-800.082041
3.5	-800.086839	-800.085662
4.0	-800.085256	-800.084938
4.5	-800.083455	-800.083329

E/Hartree

Figure B.2.4 Calculated potential energy curves



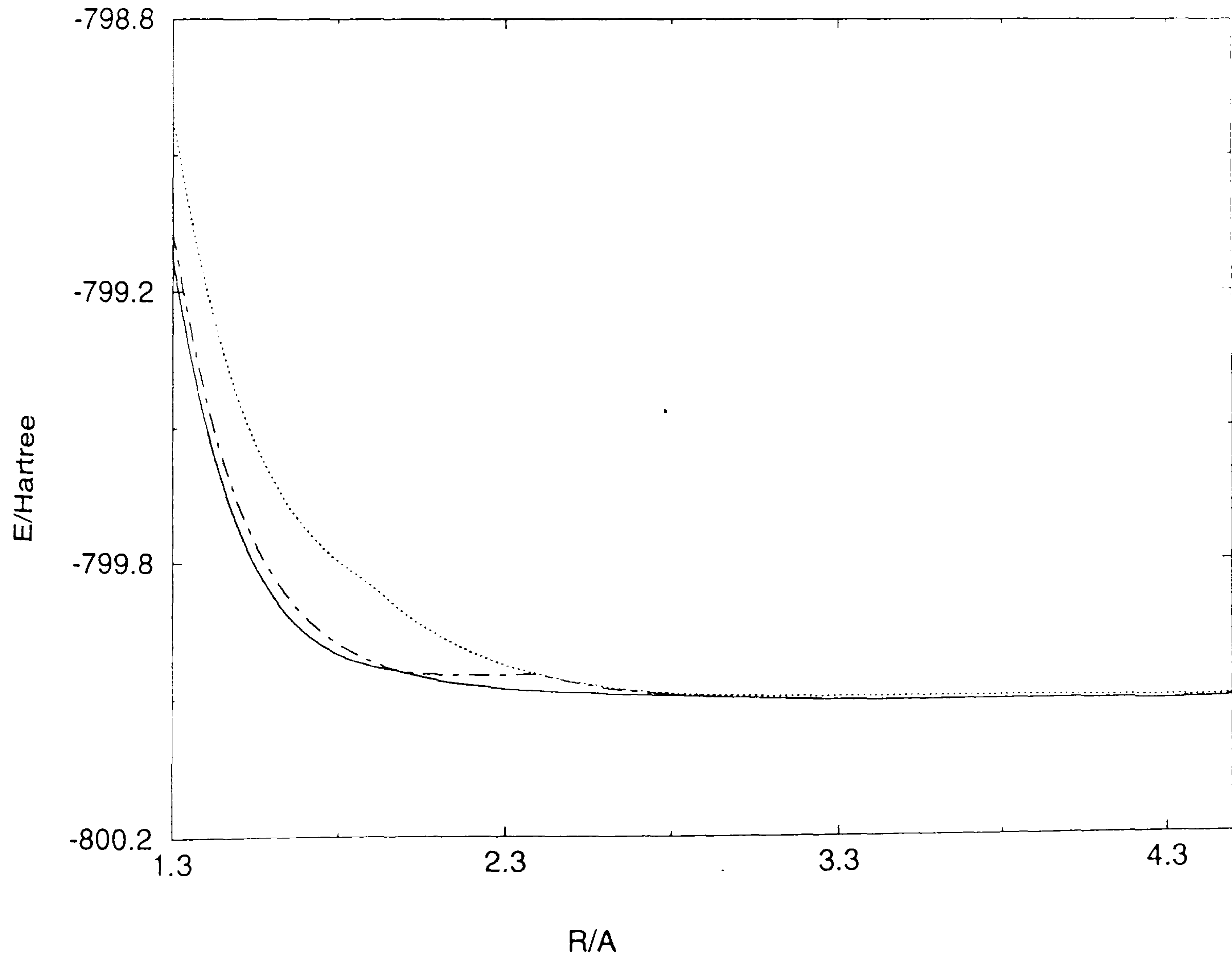
B.2.5 The CI results for the $^2\Sigma^-$ states of PCl^+ with the VDZ basis sets

Table B.2.5 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.3	-799.186805	-799.135712	-798.927318
1.5	-799.687079	-799.642704	-799.449685
1.6	-799.806119	-799.768151	-799.590771
1.7	-799.876647	-799.847169	-799.685159
1.8	-799.916393	-799.897075	-799.745402
1.9	-799.937363	-799.928860	-799.791364
2.0	-799.949800	-799.947907	-799.841716
2.1	-799.963762	-799.952623	-799.882394
2.2	-799.973260	-799.954405	-799.913685
2.25	-799.976852	-799.954725	-799.926402
2.3	-799.979868	-799.954837	-799.937456
2.4	-799.984411	-799.955589	-799.954285
2.5	-799.987903	-799.969148	-799.967748
2.75	-799.993631	-799.989576	-799.987859
3.0	-799.998941	-799.998899	-799.994605
3.5	-800.003805	-800.003584	-799.996863
4.0	-800.003261	-800.003121	-799.997497
4.5	-800.002187	-800.002102	-799.997997

E/Hartree

Figure B.2.5 Calculated potential energy curves



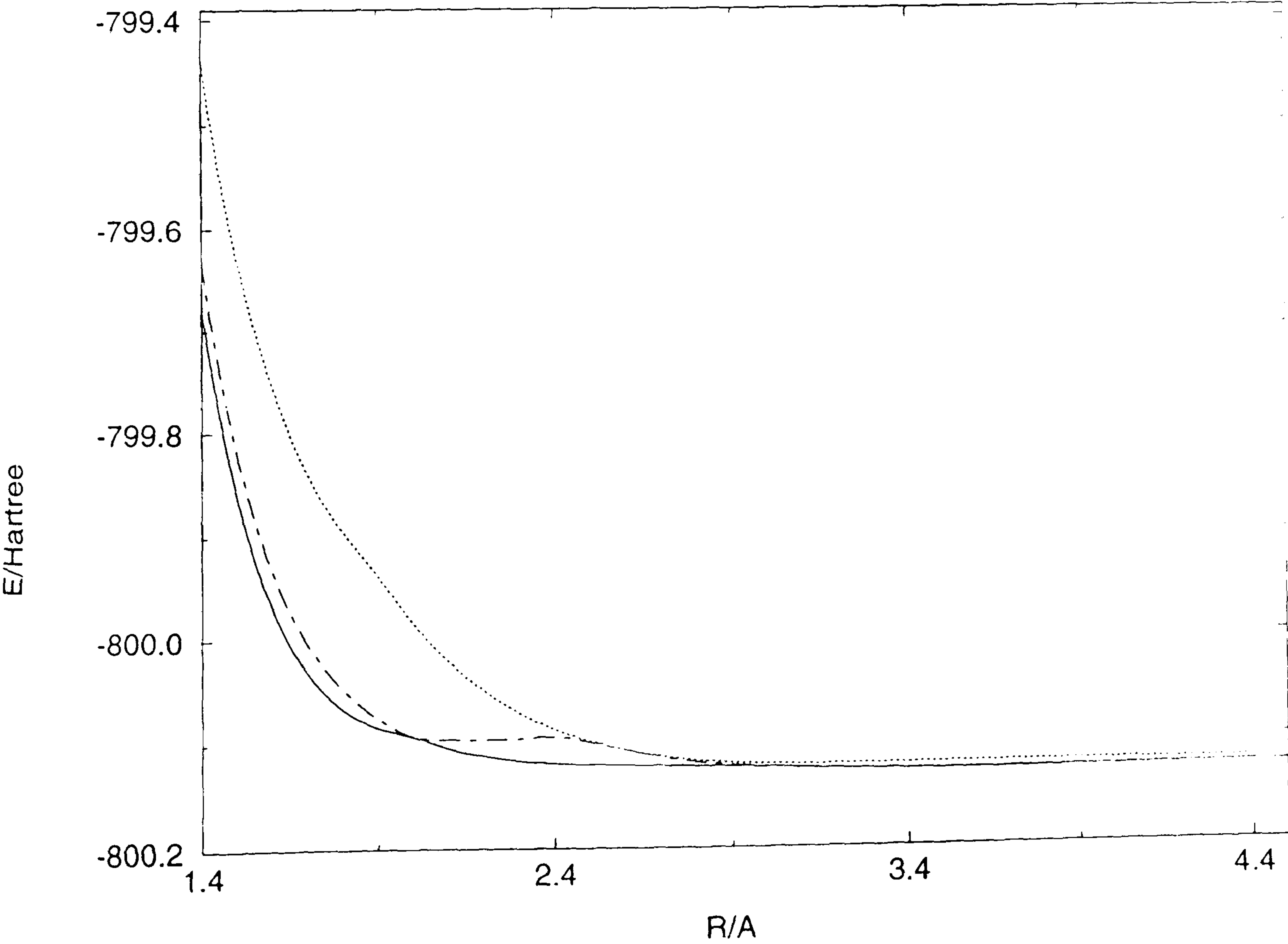
B.2.6 The CI results for the $^2\Sigma^-$ states of PCI^+ with the VTZ basis sets

Table B.2.6 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.4	-799.635237	-799.590730	-799.394912
1.5	-799.815313	-799.773983	-799.585570
1.6	-799.924592	-799.888640	-799.709778
1.7	-799.988267	-799.959903	-799.796366
1.8	-800.023294	-800.004232	-799.851358
1.9	-800.041092	-800.032007	-799.894743
2.0	-800.049978	-800.049567	-799.940918
2.1	-800.061629	-800.052718	-799.978119
2.2	-800.069160	-800.053217	-800.006716
2.3	-800.073957	-800.052430	-800.028307
2.4	-800.076943	-800.051154	-800.044312
2.5	-800.078356	-800.056973	-800.055706
2.75	-800.080375	-800.074520	-800.073092
3.0	-800.082355	-800.082018	-800.078896
3.5	-800.085574	-800.085377	-800.079358
4.0	-800.084889	-800.084762	-800.079463
4.5	-800.083745	-800.083669	-800.079688

E/Hartree

Figure B.2.6 Calculated potential energy curves



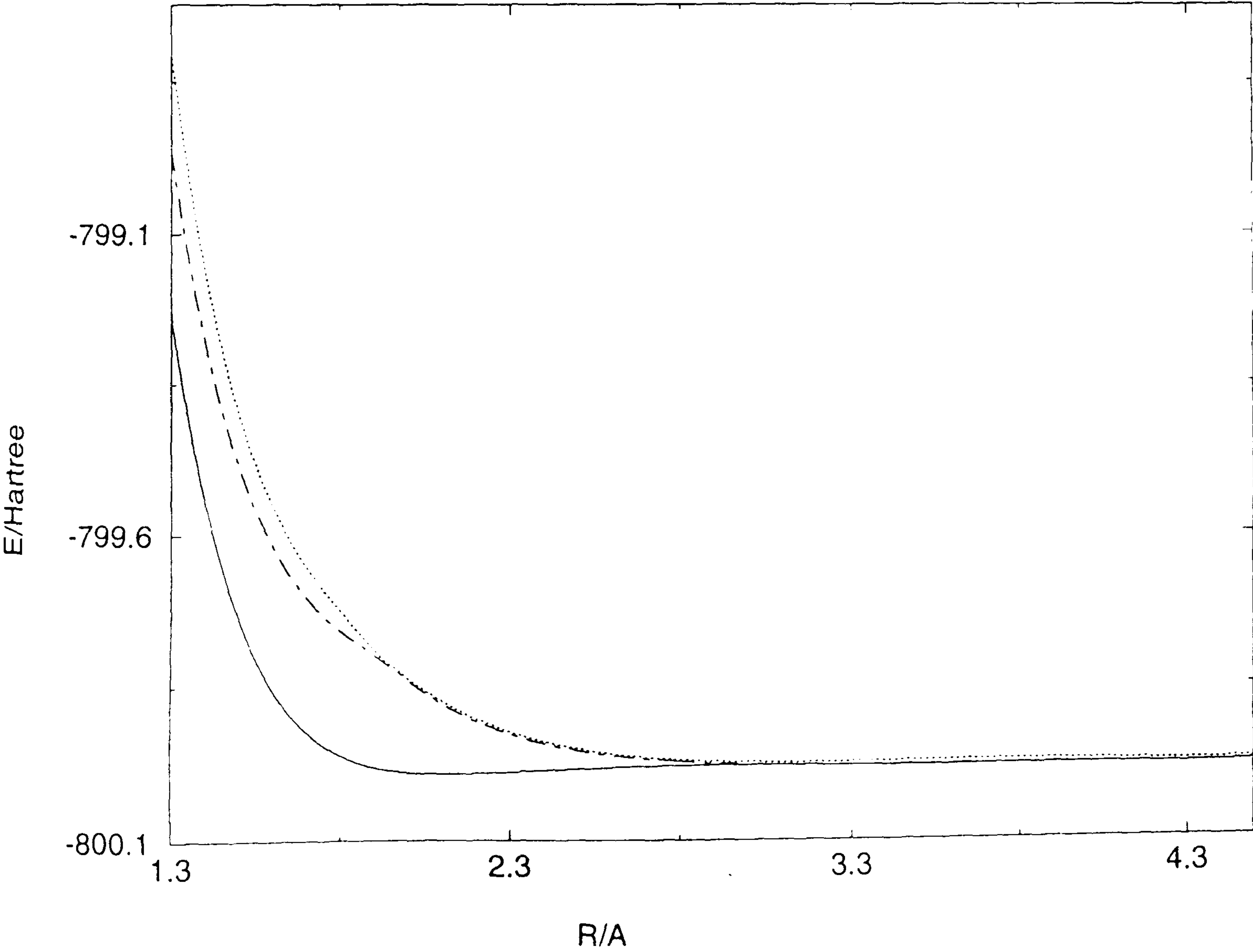
B.2.7 The CI results for the $^4\Sigma^-$ states of PCl^+ with the VDZ basis sets

Table B.2.7 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.3	-799.259477	-798.985917	-798.826456
1.5	-799.759913	-799.504101	-799.416994
1.7	-799.947681	-799.724600	-799.673549
1.8	-799.986422	-799.780650	-799.746719
1.9	-800.006336	-799.819797	-799.811240
2.0	-800.014954	-799.862526	-799.859419
2.1	-800.017239	-799.901402	-799.896731
2.2	-800.016373	-799.930565	-799.925993
2.25	-800.015388	-799.942220	-799.937844
2.3	-800.014240	-799.952245	-799.948092
2.4	-800.011808	-799.968204	-799.964508
2.5	-800.009519	-799.979829	-799.976541
2.75	-800.005302	-799.996426	-799.993697
3.0	-800.004048	-800.003034	-799.999241
3.5	-800.005102	-800.004882	-799.998263
4.0	-800.003596	-800.003453	-799.997785
4.5	-800.002218	-800.002132	-799.997999

E/Hartree

Figure B.2.7 Calculated potential energy curves



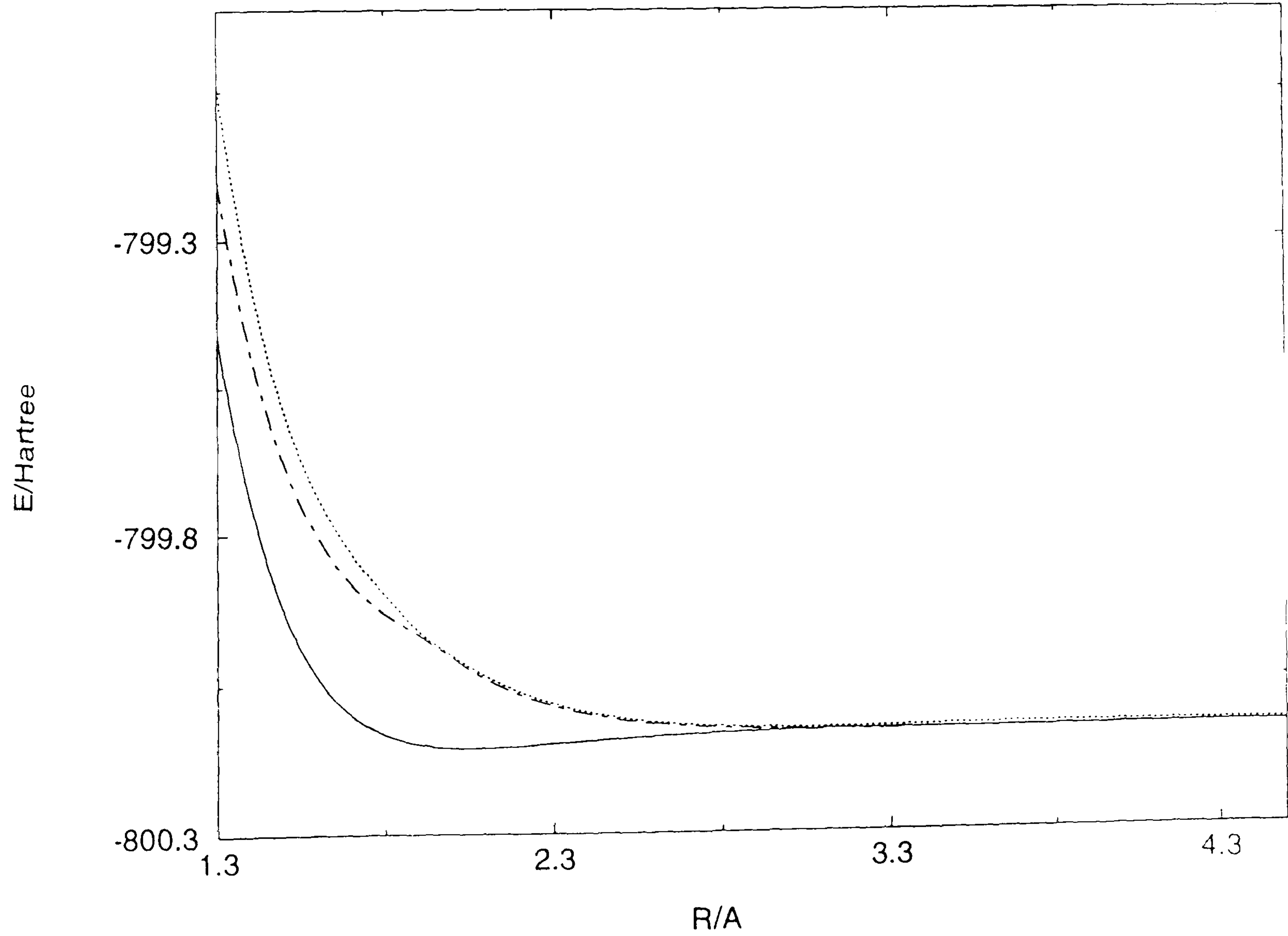
B.2.8 The CI results for the $^4\Sigma^-$ states of PCl^+ with the VTZ basis sets

Table B.2.8 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.3	-799.414763	-799.154865	-798.990817
1.5	-799.883527	-799.636160	-799.547354
1.6	-799.992500	-799.757084	-799.690631
1.8	-800.088136	-799.886147	-799.854764
1.9	-800.104843	-799.921325	-799.914567
2.0	-800.111125	-799.961638	-799.957949
2.1	-800.111590	-799.997102	-799.992132
2.2	-800.109188	-800.023554	-800.018784
2.3	-800.105691	-800.043050	-800.038761
2.4	-800.101981	-800.057204	-800.053425
2.5	-800.098460	-800.067304	-800.063984
2.75	-800.091361	-800.081011	-800.078414
3.0	-800.087503	-800.085837	-800.082742
3.5	-800.086708	-800.086524	-800.080597
4.0	-800.085164	-800.085034	-800.079695
4.5	-800.083742	-800.083667	-800.079655

E/Hartree

Figure B.2.8 Calculated potential energy curves



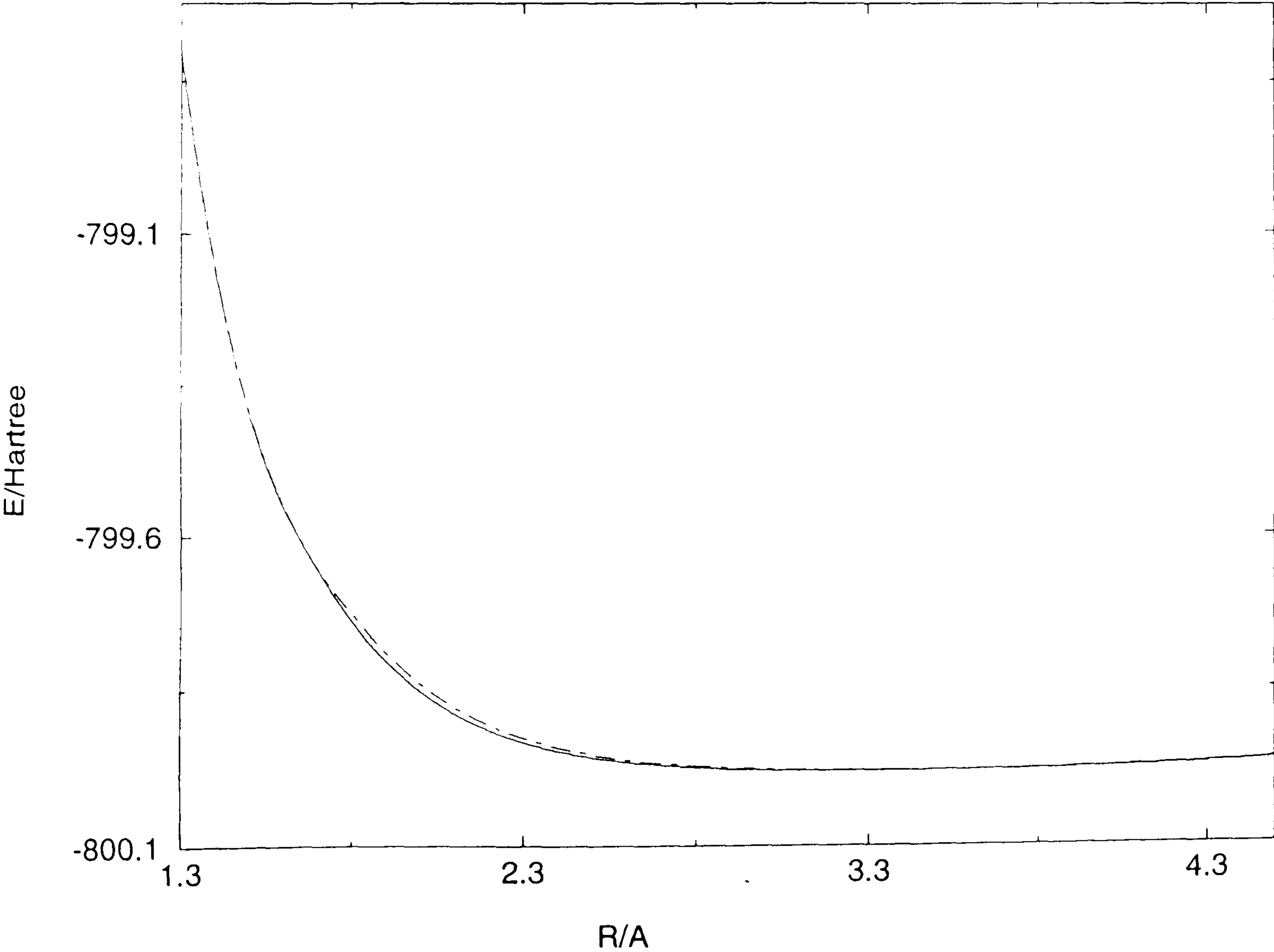
B.2.9 The CI results for the $^4\Sigma^+$ states of PCl^+ with the VDZ basis sets

Table B.2.9 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-798.826871	-798.822004
1.5	-799.418458	-799.412352
1.6	-799.573218	-799.569152
1.7	-799.676405	-799.674439
1.8	-799.760340	-799.747766
1.9	-799.825759	-799.811892
2.0	-799.875115	-799.862770
2.1	-799.912042	-799.901509
2.2	-799.939440	-799.930613
2.25	-799.950293	-799.942250
2.3	-799.959570	-799.952259
2.4	-799.974198	-799.968197
2.5	-799.984699	-799.979811
2.75	-799.999264	-799.996416
3.0	-800.004665	-800.003037
3.5	-800.005372	-800.004812
4.0	-800.001591	-800.001359
4.5	-799.990012	-799.989895

E/Hartree

Figure B.2.9 Calculated potential energy curves



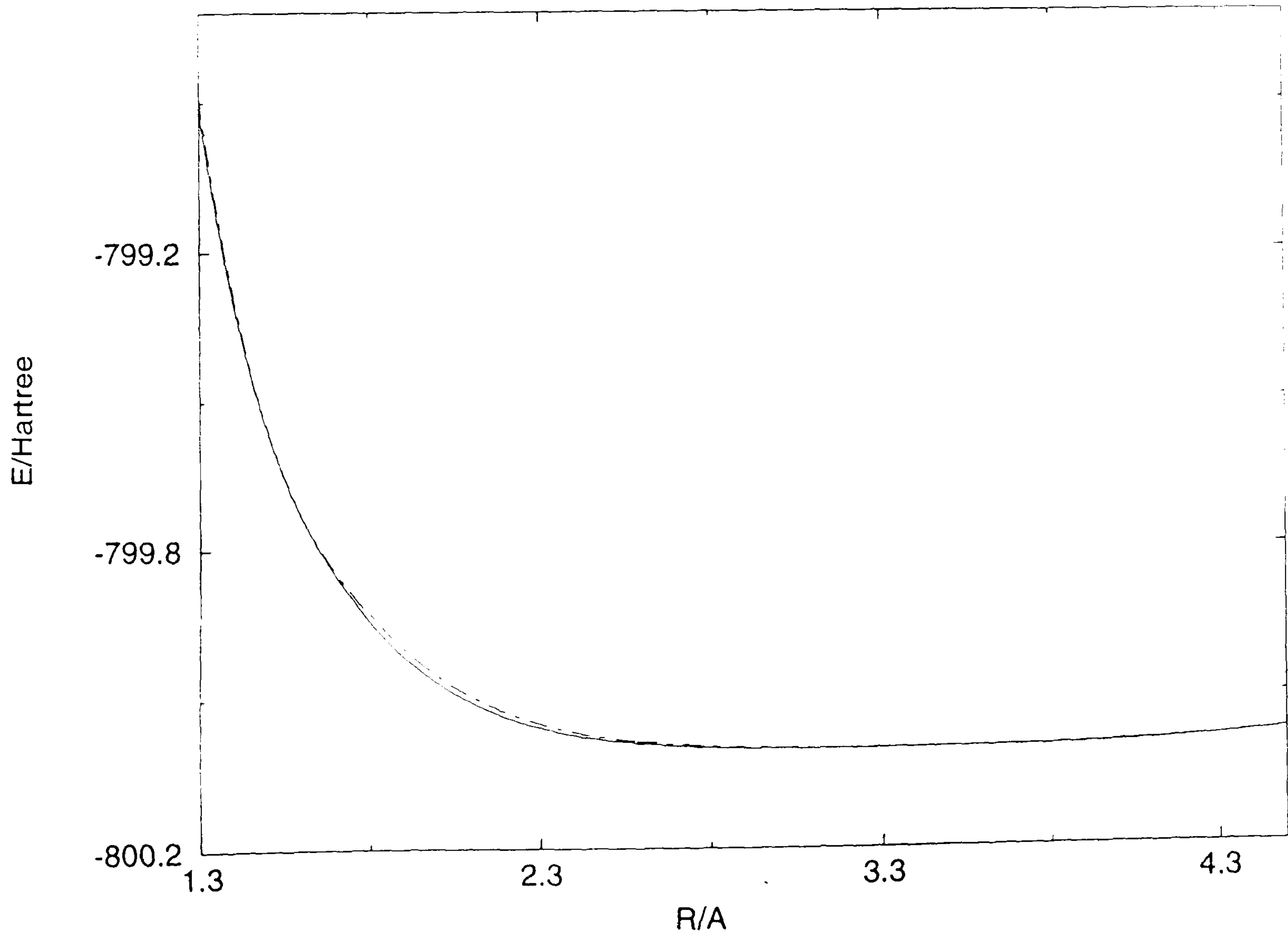
B.2.10 The CI results for the $^4\Sigma^+$ states of PCl^+ with the VTZ basis sets

Table B.2.10 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-799.010076	-798.989908
1.5	-799.548903	-799.545065
1.6	-799.693219	-799.691097
1.7	-799.791588	-799.787172
1.8	-799.869409	-799.856590
1.9	-799.929121	-799.915768
2.0	-799.973956	-799.962147
2.1	-800.007378	-799.997347
2.2	-800.032036	-800.023676
2.3	-800.049979	-800.043098
2.4	-800.062816	-800.057209
2.5	-800.071822	-800.067289
2.75	-800.083611	-800.081011
3.0	-800.087334	-800.085859
3.5	-800.086772	-800.086260
4.0	-800.081819	-800.081602
4.5	-800.061928	-800.061817

E/Hartree

Figure B.2.10 Calculated potential energy curves



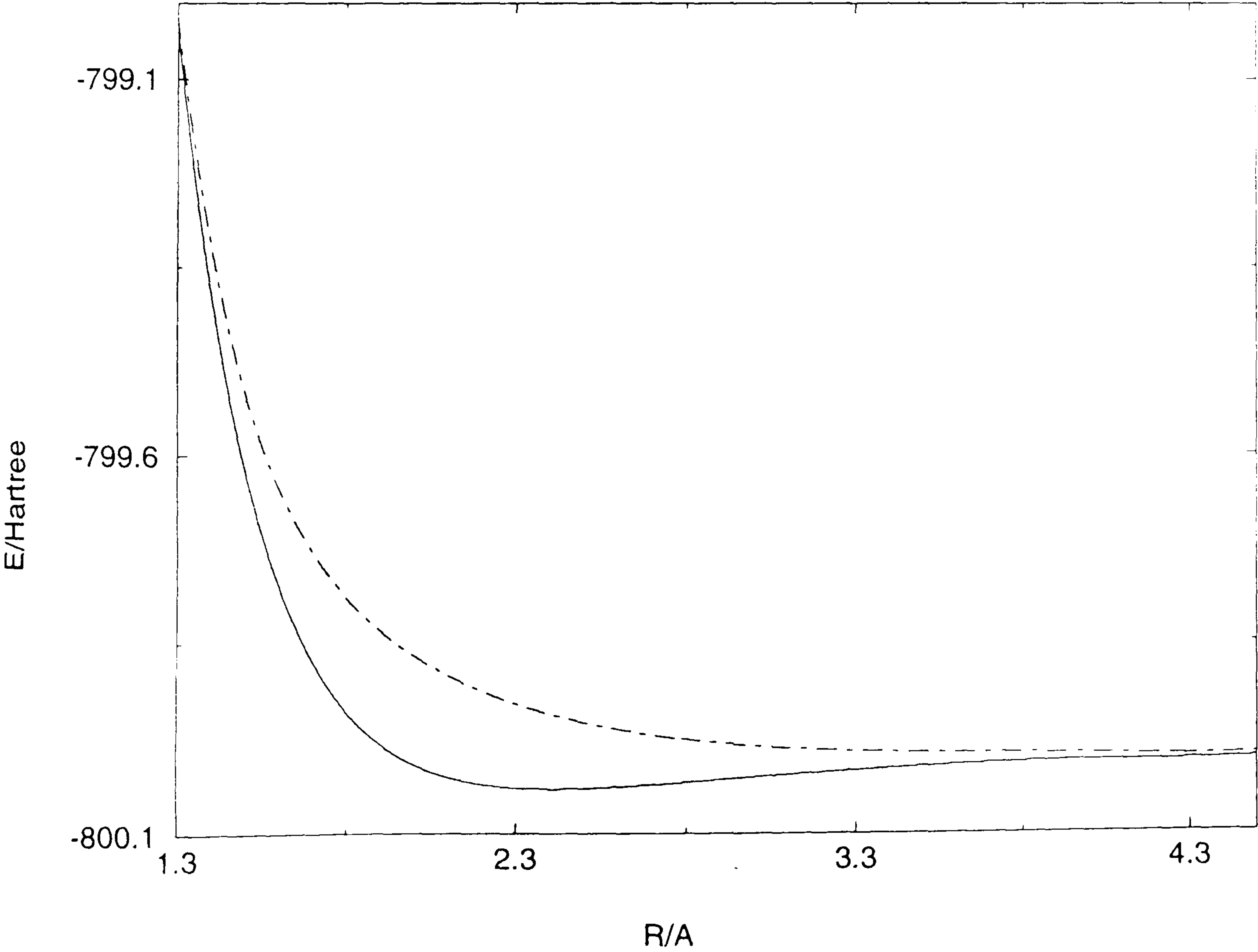
B.2.11 The CI results for the $^4\Pi$ states of PCI^+ with the VDZ basis sets

Table B.2.11 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-799.032512	-799.019368
1.5	-799.617727	-799.514403
1.6	-799.772202	-799.641548
1.7	-799.873722	-799.727757
1.8	-799.939959	-799.788288
1.9	-799.982674	-799.832333
2.0	-800.009673	-799.865563
2.1	-800.026130	-799.891494
2.2	-800.035494	-799.912277
2.25	-800.038276	-799.921164
2.3	-800.040093	-799.929201
2.4	-800.041518	-799.943061
2.5	-800.040874	-799.954410
2.75	-800.034662	-799.974368
3.0	-800.026482	-799.985810
3.5	-800.013129	-799.995106
4.0	-800.005961	-799.997356
4.5	-800.002112	-799.997303

E/Hartree

Figure B.2.11 Calculated potential energy curves



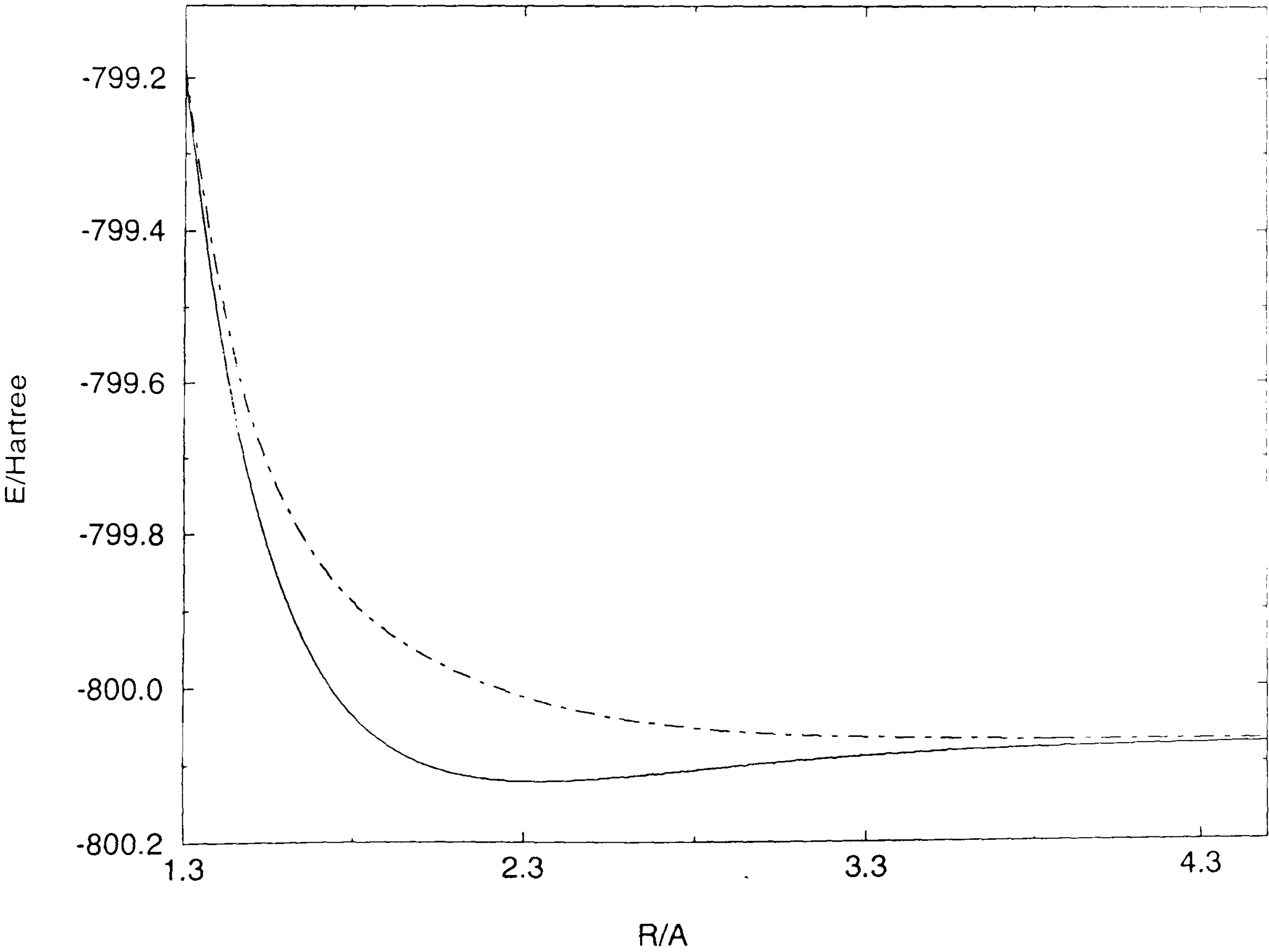
B.2.12 The CI results for the $^4\Pi$ states of PCl^+ with the VTZ basis sets

Table B.2.12 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-799.203239	-799.191663
1.5	-799.747100	-799.656065
1.6	-799.890594	-799.769278
1.7	-799.984056	-799.844568
1.8	-800.044408	-799.896889
1.9	-800.082783	-799.934967
2.0	-800.106496	-799.963922
2.1	-800.120368	-799.986773
2.2	-800.127602	-800.005274
2.3	-800.130368	-800.020418
2.4	-800.130167	-800.032803
2.5	-800.128062	-800.042868
2.75	-800.118865	-800.060199
3.0	-800.108761	-800.069800
3.5	-800.094320	-800.077393
4.0	-800.087346	-800.079154
4.5	-800.083342	-800.078657

E/Hartree

Figure B.2.12 Calculated potential energy curves



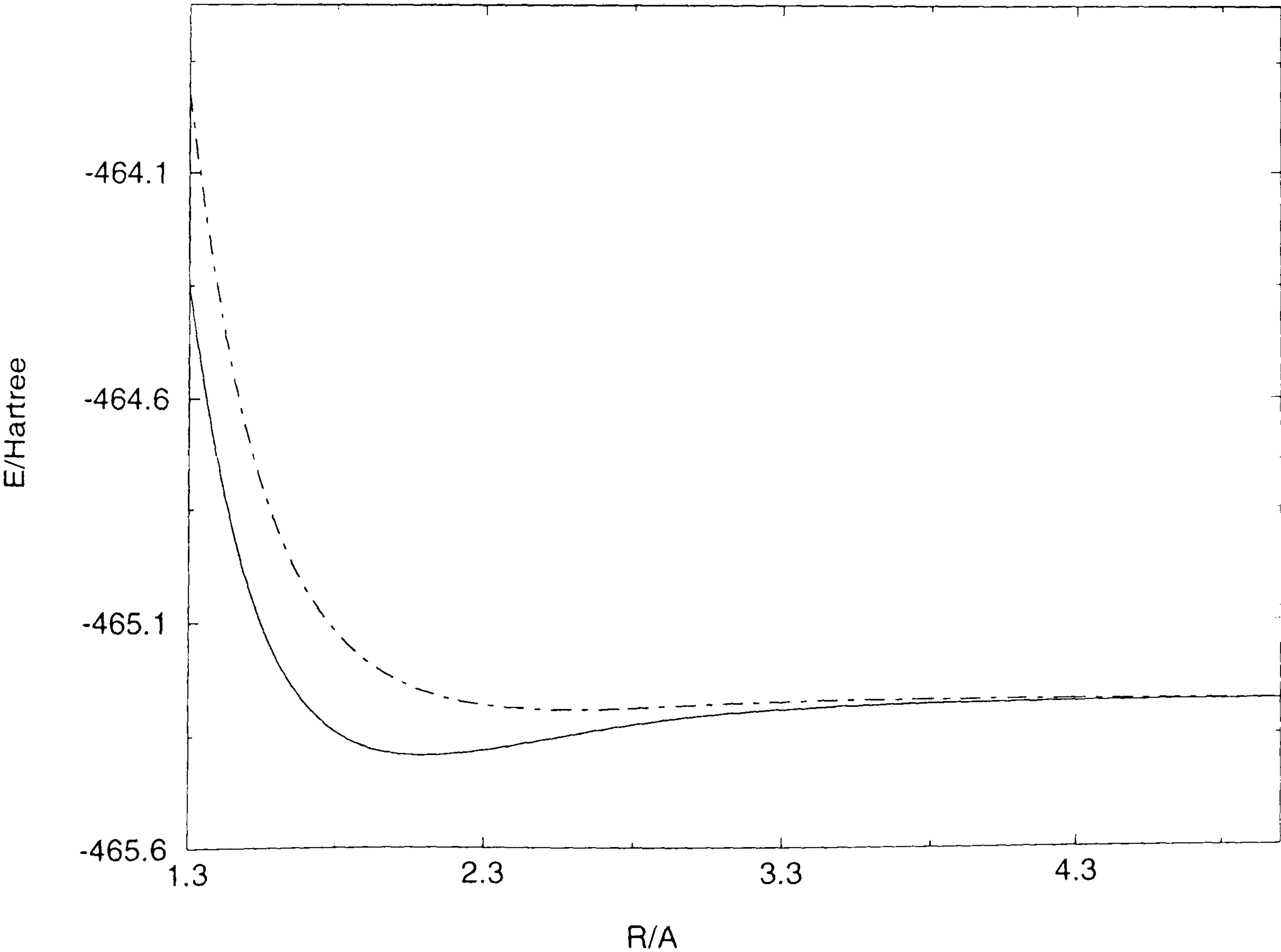
B.3.1 The CI results for the $^2\Pi$ states of AsCl^+ with the VDZ basis sets

Table B.3.1 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-464.393022	-463.966032
1.5	-465.061428	-464.729998
1.7	-465.330593	-465.076034
1.8	-465.391096	-465.169200
1.9	-465.424317	-465.231968
2.0	-465.439710	-465.274187
2.1	-465.443502	-465.302324
2.2	-465.439901	-465.320711
2.3	-465.431806	-465.332288
2.4	-465.421238	-465.339068
2.5	-465.409614	-465.342448
2.6	-465.397928	-465.343418
2.7	-465.386867	-465.342707
2.8	-465.376874	-465.340881
3.0	-465.360817	-465.335660
3.5	-465.339019	-465.325499
4.0	-465.330254	-465.322433
4.5	-465.326661	-465.321883
5.0	-465.325123	-465.321960

E/Hartree

Figure B.3.1 Calculated potential energy curves



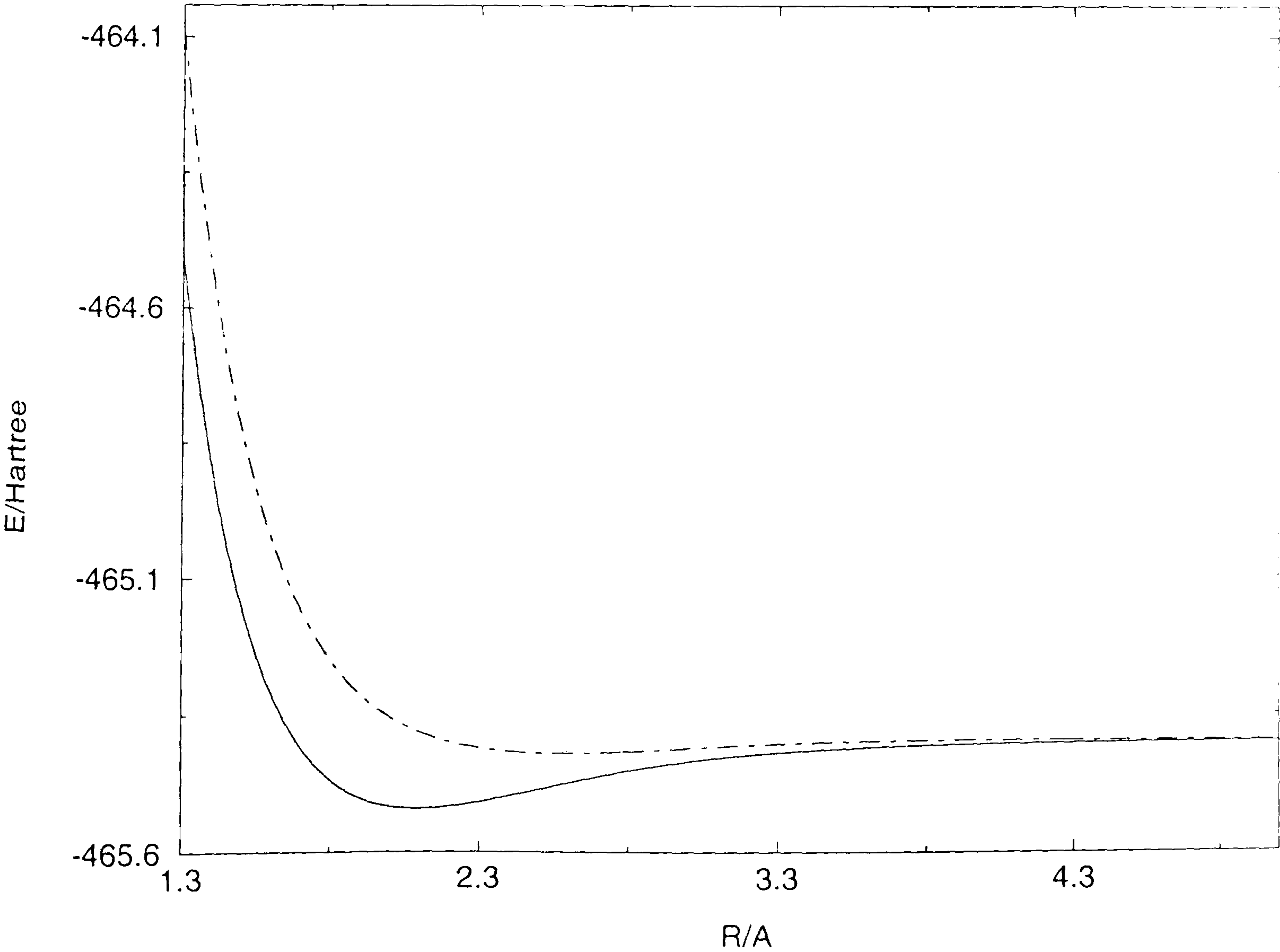
B.3.2 The CI results for the $^2\Pi$ states of AsCl^+ with the VTZ basis sets

Table B.3.2 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-464.459982	-464.044792
1.4	-464.851723	-464.482444
1.5	-465.105252	-464.778236
1.6	-465.267040	-464.978428
1.7	-465.368452	-465.114761
1.8	-465.429299	-465.207875
1.9	-465.462987	-465.270977
2.0	-465.478537	-465.313239
2.1	-465.482197	-465.341085
2.2	-465.478278	-465.358965
2.3	-465.469755	-465.369939
2.4	-465.458693	-465.376114
2.5	-465.446545	-465.378949
2.6	-465.434333	-465.379475
2.7	-465.422766	-465.378438
2.8	-465.412308	-465.376397
3.0	-465.395529	-465.370955
3.5	-465.373325	-465.360387
4.0	-465.364794	-465.357131
4.5	-465.361346	-465.356535
5.0	-465.359837	-465.356589

E/Hartree

Figure B.3.2 Calculated potential energy curves



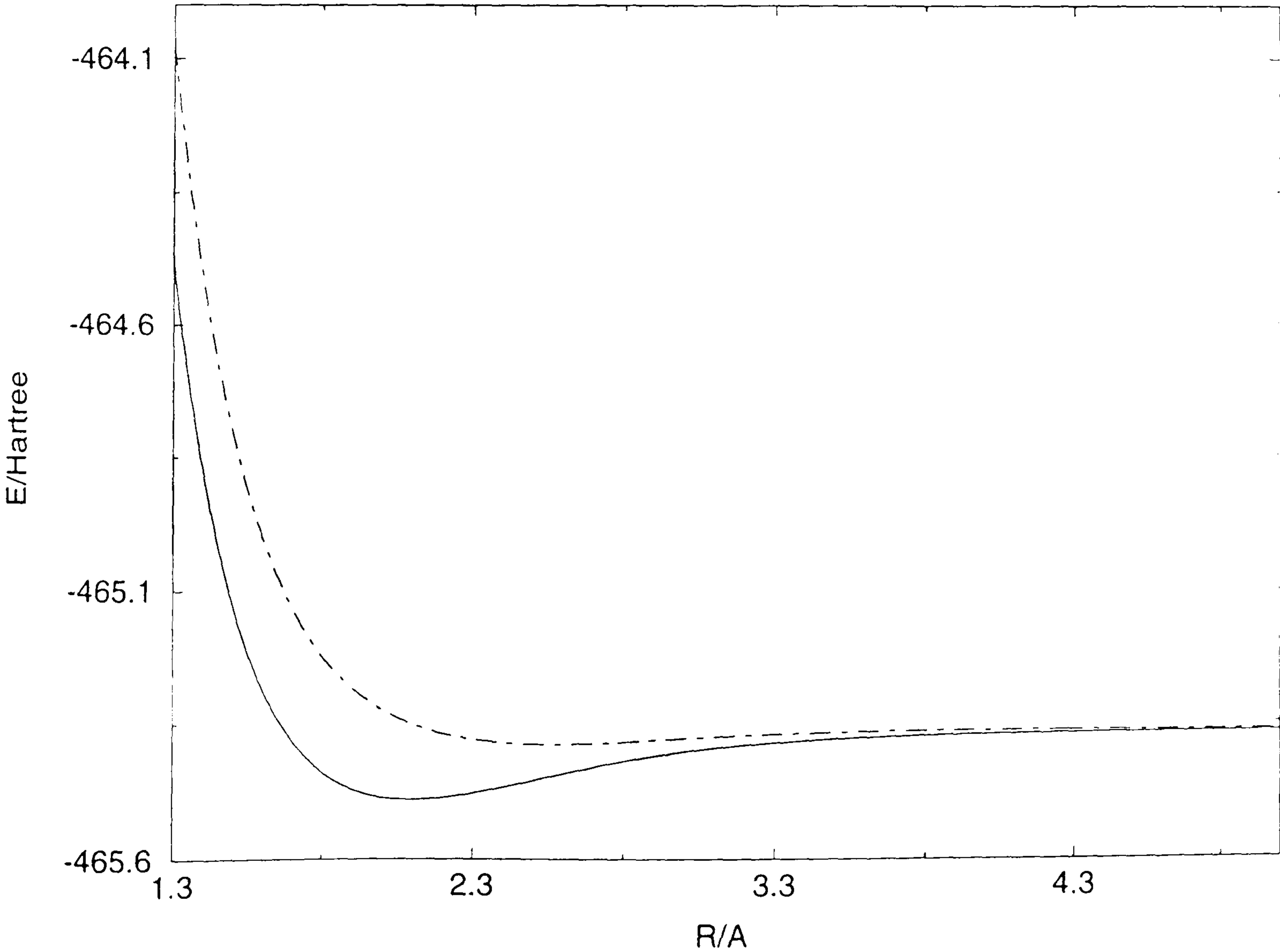
B.3.3 The CI results for the $^2\Pi$ states of AsCl^+ with the VQZ basis sets

Table B.3.3 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-464.482131	-464.072420
1.4	-464.870397	-464.504494
1.5	-465.121765	-464.797853
1.6	-465.281170	-464.995119
1.7	-465.380091	-465.128063
1.8	-465.438859	-465.218252
1.9	-465.471340	-465.279520
2.0	-465.486465	-465.321013
2.1	-465.490141	-465.348741
2.2	-465.486385	-465.366767
2.3	-465.478009	-465.377923
2.4	-465.467019	-465.384221
2.5	-465.454857	-465.387096
2.6	-465.442559	-465.387585
2.7	-465.430855	-465.386452
2.8	-465.420230	-465.384275
3.0	-465.403102	-465.378512
3.5	-465.380291	-465.367289
4.0	-465.371455	-465.363692
4.5	-465.367846	-465.362948
5.0	-465.366251	-465.362932

E/Hartree

Figure B.3.3 Calculated potential energy curves



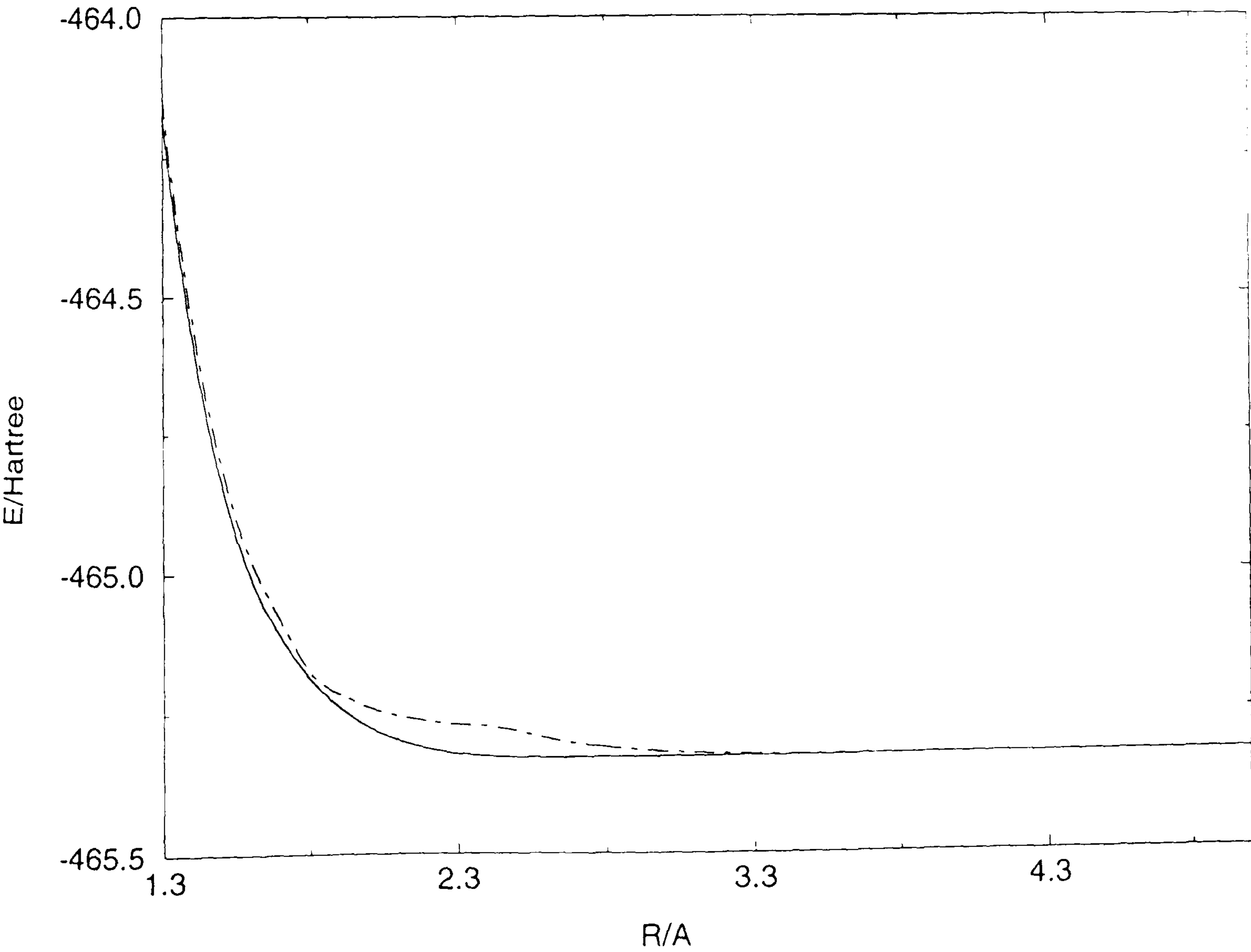
B.3.4 The CI results for the $^2\Sigma^+$ states of AsCl^+ with the VDZ basis sets

Table B.3.4 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-464.173184	-464.141024
1.4	-464.574885	-464.542889
1.5	-464.837007	-464.805336
1.6	-465.004458	-464.973424
1.7	-465.109646	-465.080266
1.8	-465.185175	-465.173437
1.9	-465.237363	-465.213561
2.0	-465.273149	-465.238203
2.1	-465.296978	-465.253412
2.2	-465.312099	-465.262906
2.3	-465.321033	-465.268889
2.4	-465.325761	-465.272695
2.5	-465.328066	-465.281802
2.6	-465.328607	-465.294645
2.7	-465.328517	-465.304128
2.8	-465.328296	-465.311059
3.0	-465.328122	-465.319651
3.5	-465.327919	-465.326287
4.0	-465.326796	-465.326365
4.5	-465.325613	-465.325449
5.0	-465.324788	-465.324705

E/Hartree

Figure B.3.4 Calculated potential energy curves



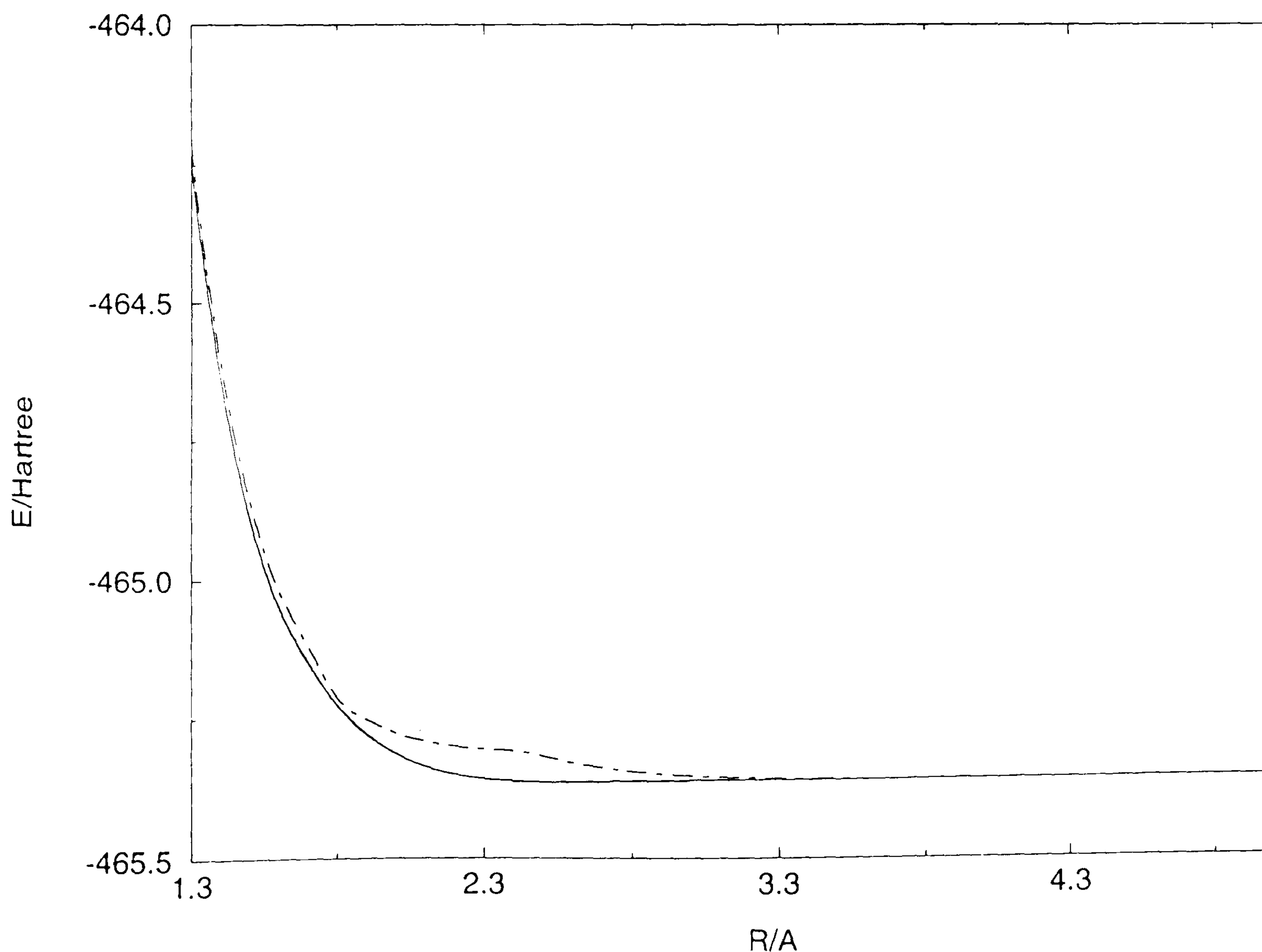
B.3.5 The CI results for the $^2\Sigma^+$ states of AsCl^+ with the VTZ basis sets

Table B.3.5 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-464.241841	-464.211159
1.4	-464.629994	-464.599193
1.5	-464.882680	-464.851924
1.6	-465.045307	-465.014771
1.7	-465.148819	-465.118872
1.8	-465.225555	-465.212084
1.9	-465.278470	-465.252176
2.0	-465.314009	-465.276655
2.1	-465.337067	-465.291554
2.2	-465.351252	-465.300639
2.3	-465.359261	-465.306159
2.4	-465.363146	-465.309482
2.5	-465.364804	-465.318395
2.6	-465.364726	-465.330696
2.7	-465.364154	-465.339777
2.8	-465.363584	-465.346422
3.0	-465.363036	-465.354674
3.5	-465.362622	-465.361022
4.0	-465.361481	-465.361052
4.5	-465.360331	-465.360165
5.0	-465.359518	-465.359433

E/Hartree

Figure B.3.5 Calculated potential energy curves



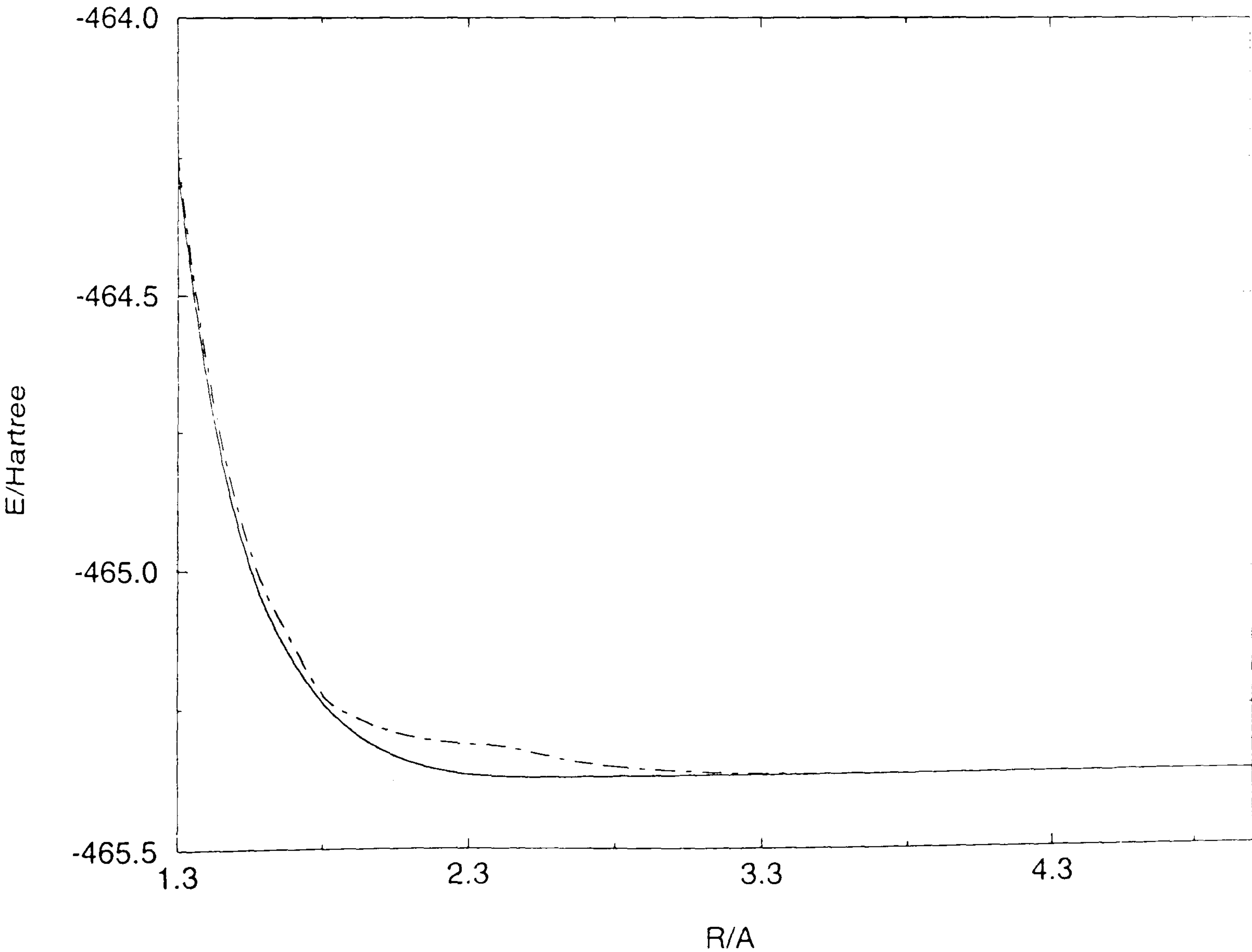
B.3.6 The CI results for the $^2\Sigma^+$ states of AsCl^+ with the VQZ basis sets

Table B.3.6 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-464.265602	-464.235427
1.4	-464.649462	-464.619139
1.5	-464.899419	-464.869108
1.6	-465.059563	-465.029446
1.7	-465.160725	-465.131380
1.8	-465.236603	-465.222088
1.9	-465.288196	-465.260970
2.0	-465.323045	-465.284837
2.1	-465.345864	-465.299505
2.2	-465.359988	-465.308551
2.3	-465.367943	-465.314103
2.4	-465.371723	-465.317468
2.5	-465.373246	-465.326660
2.6	-465.372978	-465.338834
2.7	-465.372206	-465.347765
2.8	-465.371442	-465.354249
3.0	-465.370553	-465.362186
3.5	-465.369562	-465.367959
4.0	-465.368121	-465.367688
4.5	-465.366820	-465.366652
5.0	-465.365931	-465.365845

E/Hartree

Figure B.3.6 Calculated potential energy curves



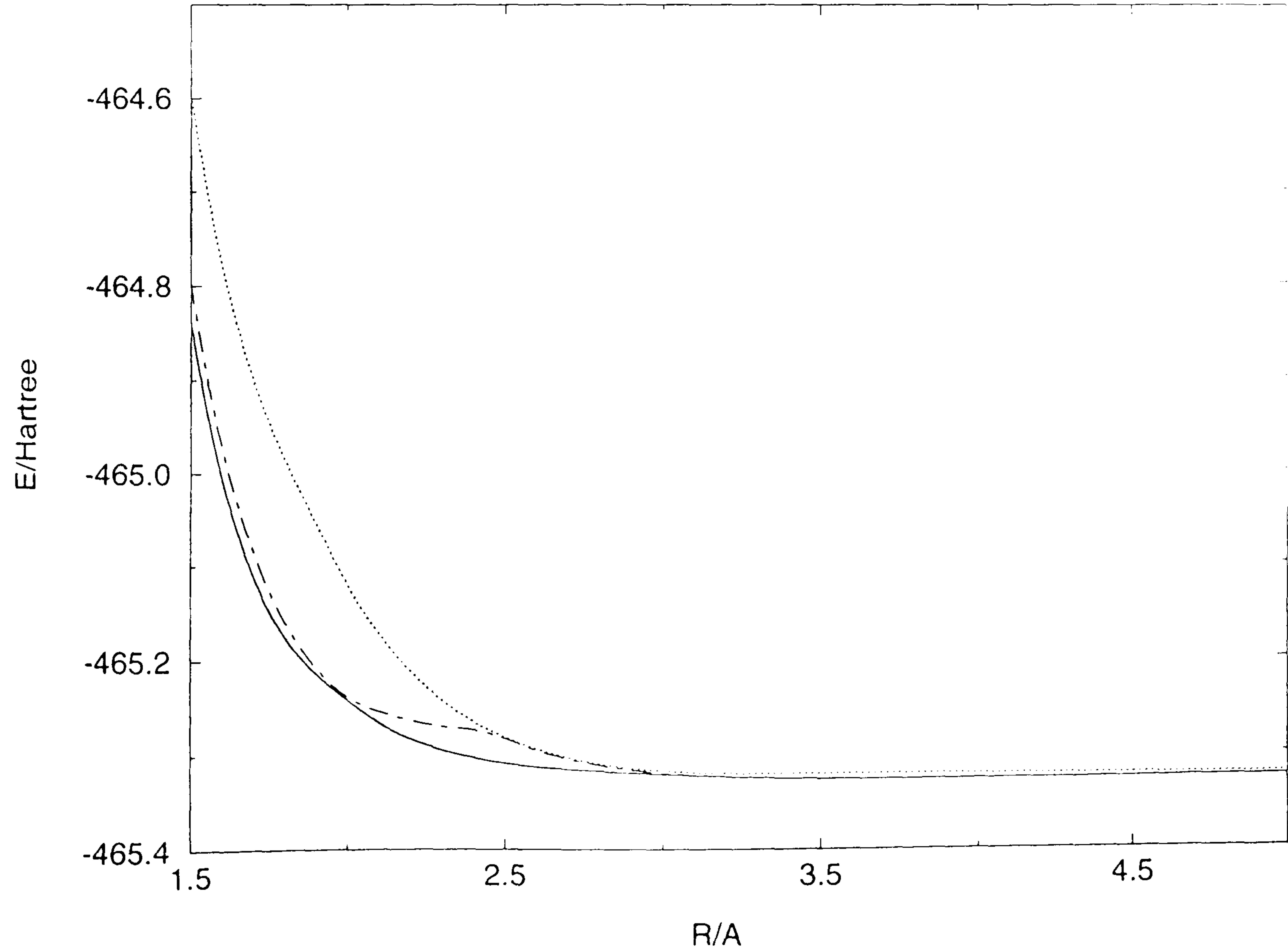
B.3.7 The CI results for the $^2\Sigma^-$ states of AsCl^+ with the VDZ basis sets

Table B.3.7 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.5	-464.836348	-464.796807	-464.594659
1.6	-465.003955	-464.970011	-464.776071
1.7	-465.109195	-465.083017	-464.898472
1.8	-465.174148	-465.157608	-464.984038
1.9	-465.213894	-465.207390	-465.053767
2.0	-465.241819	-465.238560	-465.119370
2.1	-465.265721	-465.253762	-465.171208
2.2	-465.282457	-465.263203	-465.211092
2.3	-465.294230	-465.269130	-465.241467
2.4	-465.302531	-465.272898	-465.264338
2.5	-465.308251	-465.281980	-465.280357
2.6	-465.312404	-465.294770	-465.293182
2.7	-465.315341	-465.304212	-465.302618
2.8	-465.317465	-465.311111	-465.309434
3.0	-465.320766	-465.319667	-465.317061
3.5	-465.326270	-465.326059	-465.320179
4.0	-465.326317	-465.326162	-465.320683
4.5	-465.325390	-465.325293	-465.321128
5.0	-465.324643	-465.324583	-465.321551

E/Hartree

Figure B.3.7 Calculated potential energy curves



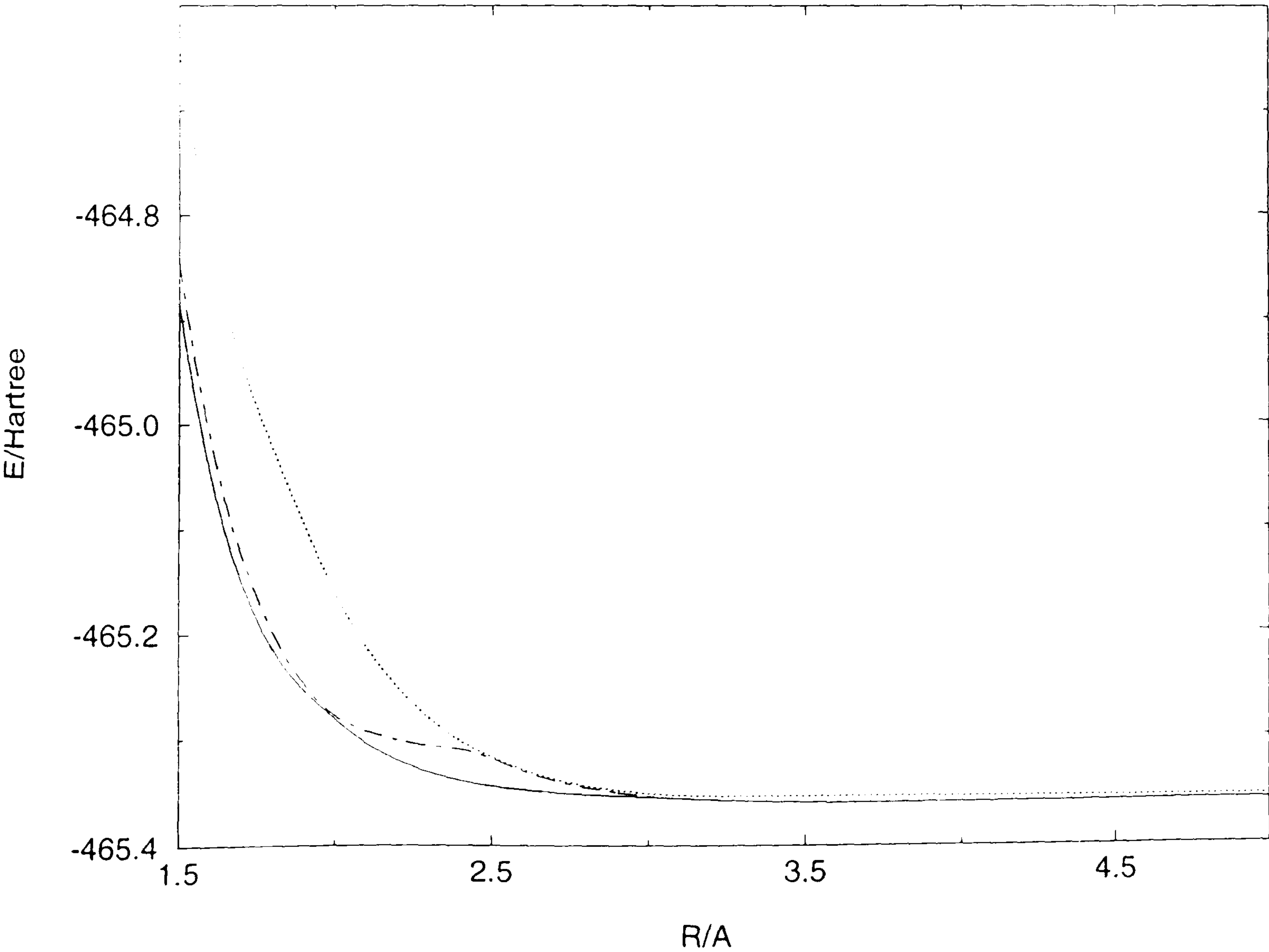
B.3.8 The CI results for the $^2\Sigma^-$ states of AsCl^+ with the VTZ basis sets

Table B.3.8 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.5	-464.881860	-464.843165	-464.640434
1.6	-465.044667	-465.011122	-464.817414
1.7	-465.148268	-465.122144	-464.938106
1.8	-465.212680	-465.196086	-465.020926
1.9	-465.252469	-465.245989	-465.093437
2.0	-465.280286	-465.277047	-465.160495
2.1	-465.303970	-465.291951	-465.211437
2.2	-465.320374	-465.300993	-465.250249
2.3	-465.331738	-465.306461	-465.279609
2.4	-465.339595	-465.309747	-465.301612
2.5	-465.344831	-465.318624	-465.316962
2.6	-465.348581	-465.330862	-465.329235
2.7	-465.351170	-465.339888	-465.338260
2.8	-465.353008	-465.346489	-465.344783
3.0	-465.355878	-465.354690	-465.352102
3.5	-465.360989	-465.360779	-465.354958
4.0	-465.360976	-465.360819	-465.355379
4.5	-465.360072	-465.359974	-465.355783
5.0	-465.359338	-465.359276	-465.356171

E/Hartree

Figure B.3.8 Calculated potential energy curves



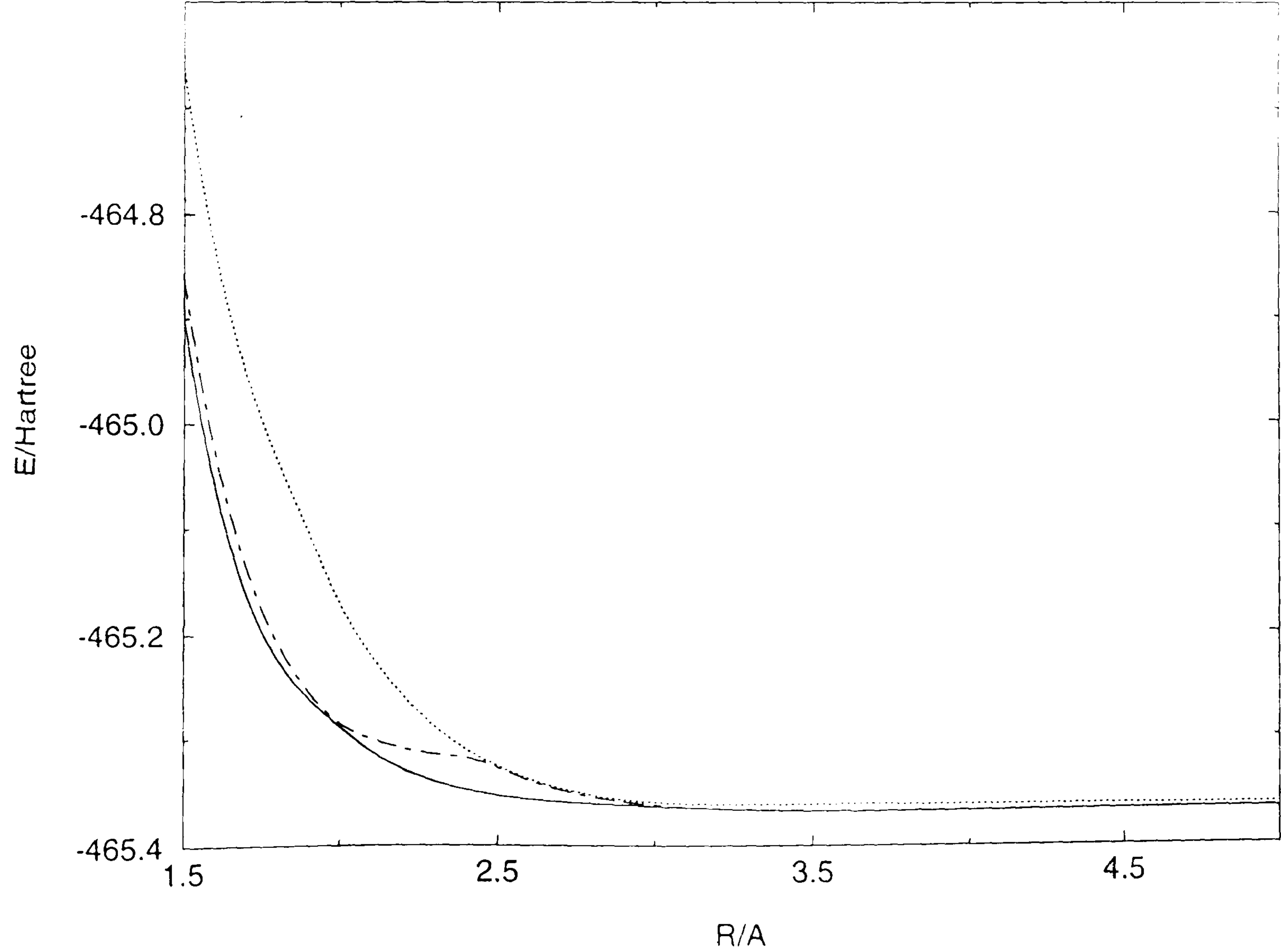
B.3.9 The CI results for the $^2\Sigma^-$ states of AsCl^+ with the VQZ basis sets

Table B.3.9 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.5	-464.898555	-464.860593	-464.661379
1.6	-465.058884	-465.026037	-464.833788
1.7	-465.160129	-465.134556	-464.951470
1.8	-465.222884	-465.206537	-465.034336
1.9	-465.261297	-465.254804	-465.103094
2.0	-465.288354	-465.285233	-465.169323
2.1	-465.311763	-465.299905	-465.219924
2.2	-465.328149	-465.308909	-465.258654
2.3	-465.339589	-465.314412	-465.287989
2.4	-465.347524	-465.317746	-465.309931
2.5	-465.352779	-465.326899	-465.325205
2.6	-465.356516	-465.339006	-465.337346
2.7	-465.359043	-465.347879	-465.346216
2.8	-465.360781	-465.354316	-465.352573
3.0	-465.363394	-465.362197	-465.359565
3.5	-465.367916	-465.367705	-465.361842
4.0	-465.367597	-465.367439	-465.361952
4.5	-465.366542	-465.366442	-465.362201
5.0	-465.365731	-465.365669	-465.362512

E/Hartree

Figure B.3.9 Calculated potential energy curves



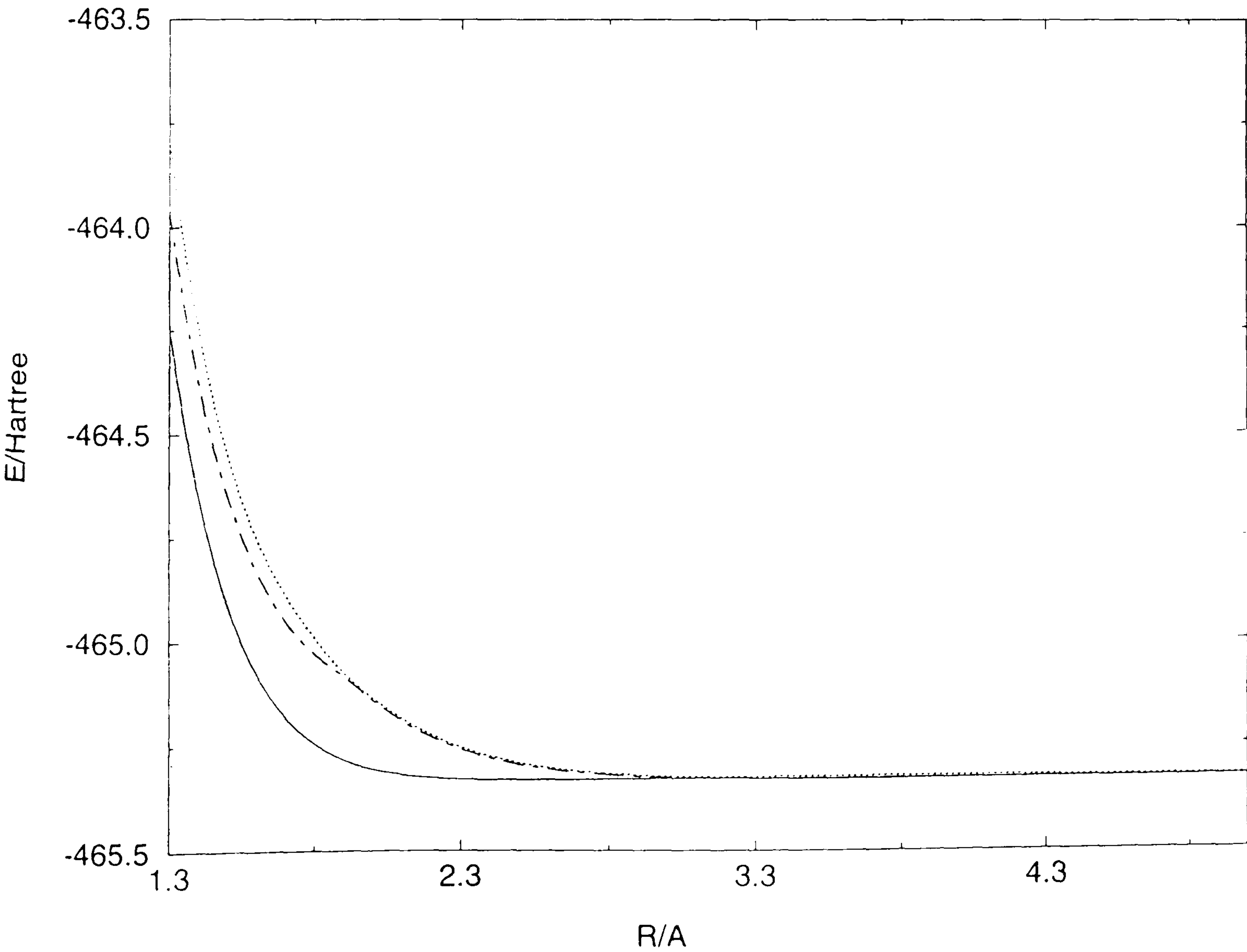
B.3.10 The CI results for the $^4\Sigma^-$ states of AsCl^+ with the VDZ basis sets

Table B.3.10 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.3	-464.239685	-463.954696	-463.786869
1.4	-464.642868	-464.367642	-464.238377
1.5	-464.905985	-464.643454	-464.544057
1.6	-465.073931	-464.826240	-464.747689
1.7	-465.178532	-464.947760	-464.884158
1.8	-465.242544	-465.027508	-464.989089
1.9	-465.281524	-465.083130	-465.074375
2.0	-465.304355	-465.140451	-465.135941
2.1	-465.317211	-465.190563	-465.184811
2.2	-465.324138	-465.228383	-465.222940
2.3	-465.327664	-465.256705	-465.251825
2.4	-465.329244	-465.277716	-465.273411
2.5	-465.329698	-465.293130	-465.289340
2.6	-465.329500	-465.304294	-465.300928
2.7	-465.328945	-465.312258	-465.309210
2.8	-465.328243	-465.317840	-465.314984
3.0	-465.327126	-465.324236	-465.321154
3.5	-465.327771	-465.327589	-465.321670
4.0	-465.326742	-465.326583	-465.321020
4.5	-465.325493	-465.325395	-465.321187
5.0	-465.324656	-465.324595	-465.321546

E/Hartree

Figure B.3.10 Calculated potential energy curves



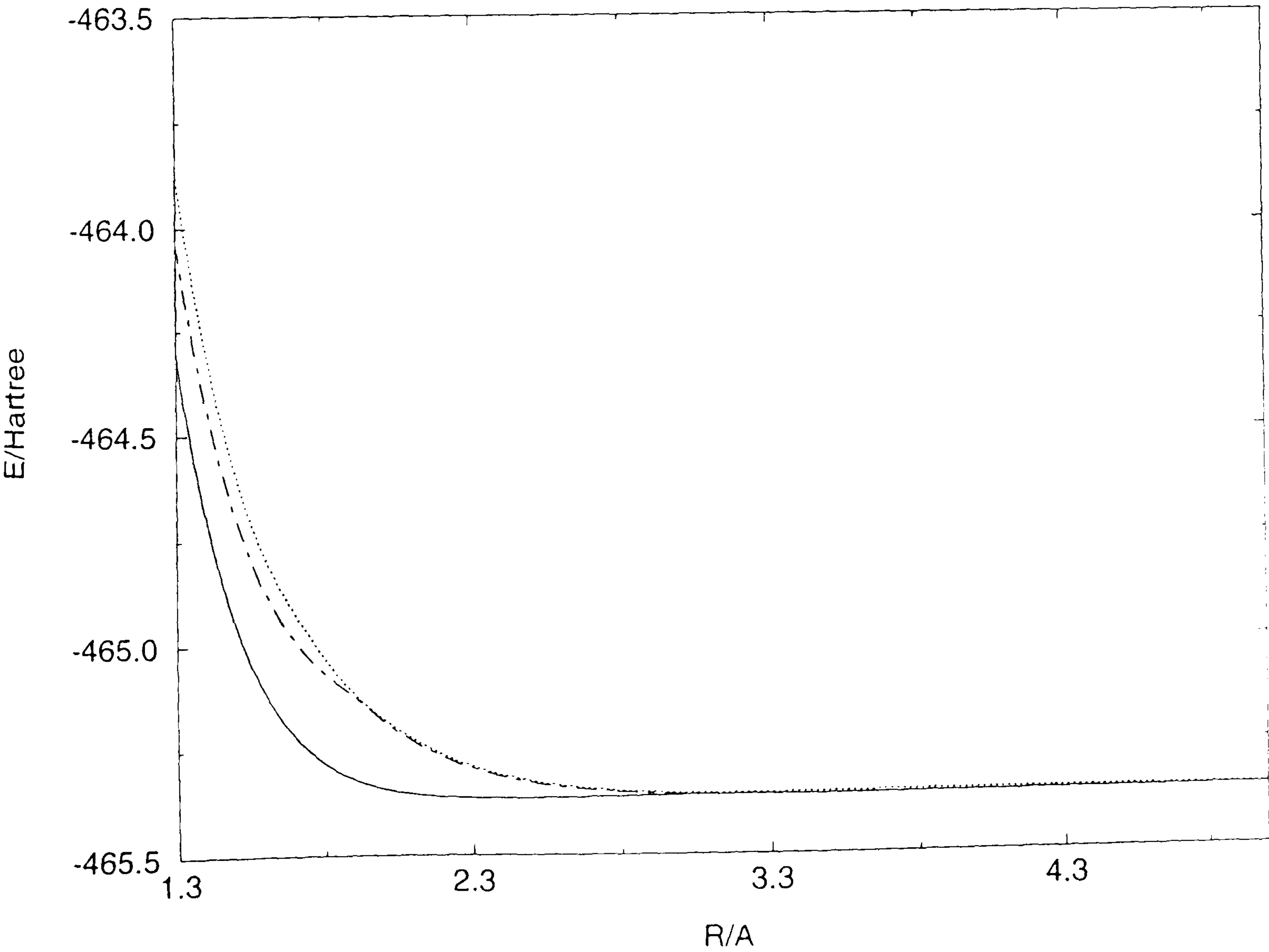
B.3.11 The CI results for the $^4\Sigma^-$ states of AsCl^+ with the VTZ basis sets

Table B.3.11 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.3	-464.306642	-464.031278	-463.865422
1.4	-464.696623	-464.429039	-464.299721
1.5	-464.950650	-464.693377	-464.593088
1.6	-465.114085	-464.869525	-464.789942
1.7	-465.217781	-464.987866	-464.921821
1.8	-465.281151	-465.067294	-465.030063
1.9	-465.320095	-465.122844	-465.116243
2.0	-465.342703	-465.181650	-465.176704
2.1	-465.355183	-465.230620	-465.224816
2.2	-465.361673	-465.267260	-465.261831
2.3	-465.364733	-465.294522	-465.289670
2.4	-465.365849	-465.314645	-465.310371
2.5	-465.365872	-465.329354	-465.325594
2.6	-465.365298	-465.339981	-465.336647
2.7	-465.364434	-465.347559	-465.344547
2.8	-465.363488	-465.352878	-465.350065
3.0	-465.362032	-465.358998	-465.356001
3.5	-465.362393	-465.362219	-465.356405
4.0	-465.361374	-465.361215	-465.355698
4.5	-465.360170	-465.360071	-465.355835
5.0	-465.359349	-465.359287	-465.356162

E/Hartree

Figure B.3.11 Calculated potential energy curves



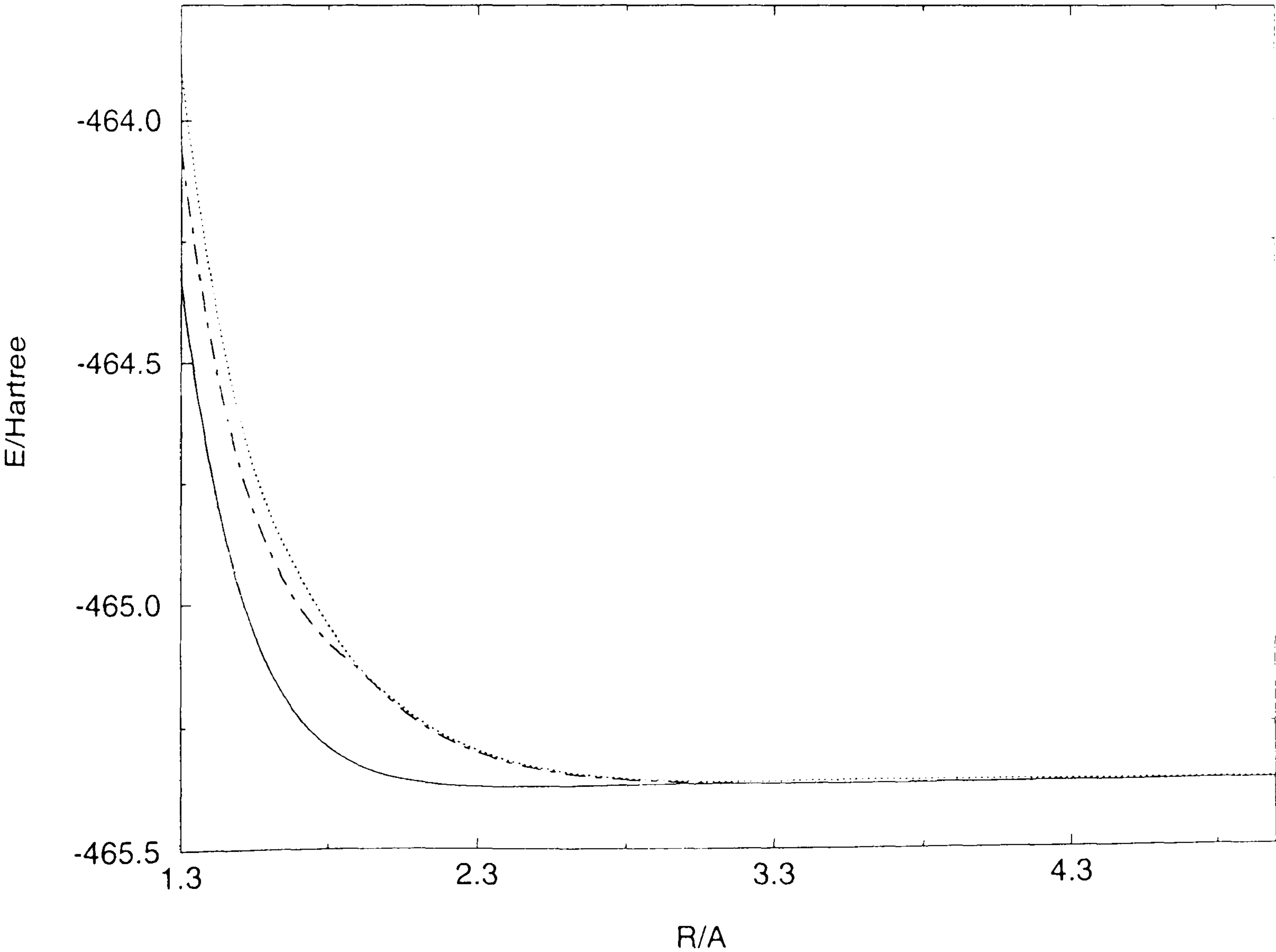
B.3.12 The CI results for the $^4\Sigma^-$ states of AsCl^+ with the VQZ basis sets

Table B.3.12 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3
1.3	-464.330006	-464.057682	-463.894277
1.4	-464.715695	-464.451346	-464.321899
1.5	-464.966975	-464.712952	-464.612311
1.6	-465.127925	-464.886112	-464.806191
1.7	-465.229284	-465.001404	-464.935204
1.8	-465.290969	-465.077931	-465.042054
1.9	-465.328765	-465.131825	-465.126386
2.0	-465.350799	-465.190658	-465.185468
2.1	-465.363050	-465.239169	-465.233297
2.2	-465.369480	-465.275669	-465.270209
2.3	-465.372541	-465.302874	-465.298001
2.4	-465.373668	-465.322929	-465.318635
2.5	-465.373685	-465.337536	-465.333755
2.6	-465.373078	-465.348034	-465.344676
2.7	-465.372151	-465.355465	-465.352425
2.8	-465.371118	-465.360630	-465.357784
3.0	-465.369453	-465.366452	-465.363409
3.5	-465.369304	-465.369132	-465.363280
4.0	-465.367991	-465.367832	-465.362273
4.5	-465.366639	-465.366539	-465.362253
5.0	-465.365743	-465.365680	-465.362503

E/Hartree

Figure B.3.12 Calculated potential energy curves



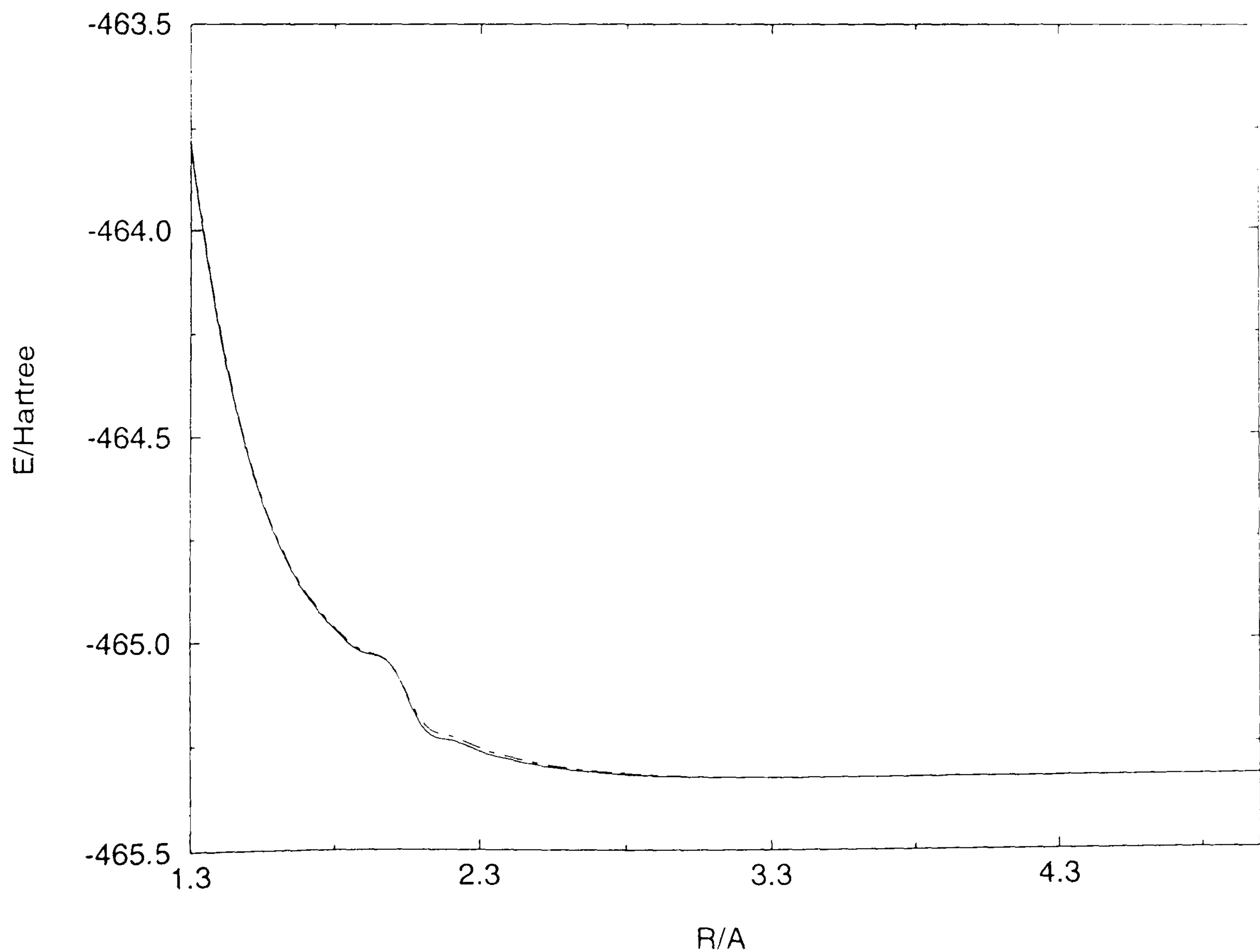
B.3.13 The CI results for the $^4\Sigma^+$ states of AsCl^+ with the VDZ basis sets

Table B.3.13 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-463.786464	-463.776302
1.4	-464.238606	-464.229595
1.5	-464.544339	-464.536291
1.6	-464.747987	-464.740836
1.7	-464.882149	-464.875842
1.8	-464.969856	-464.964350
1.9	-465.026756	-465.022109
2.0	-465.063070	-465.060048
2.1	-465.202177	-465.190715
2.2	-465.238152	-465.228470
2.3	-465.264824	-465.256746
2.4	-465.284399	-465.277727
2.5	-465.298590	-465.293123
2.6	-465.308727	-465.304278
2.7	-465.315840	-465.312238
2.8	-465.320727	-465.317822
3.0	-465.326106	-465.324225
3.5	-465.328441	-465.327776
4.0	-465.327033	-465.326756
4.5	-465.325656	-465.3255177
5.0	-465.324769	-465.3246903

E/Hartree

Figure B.3.13 Calculated potential energy curves



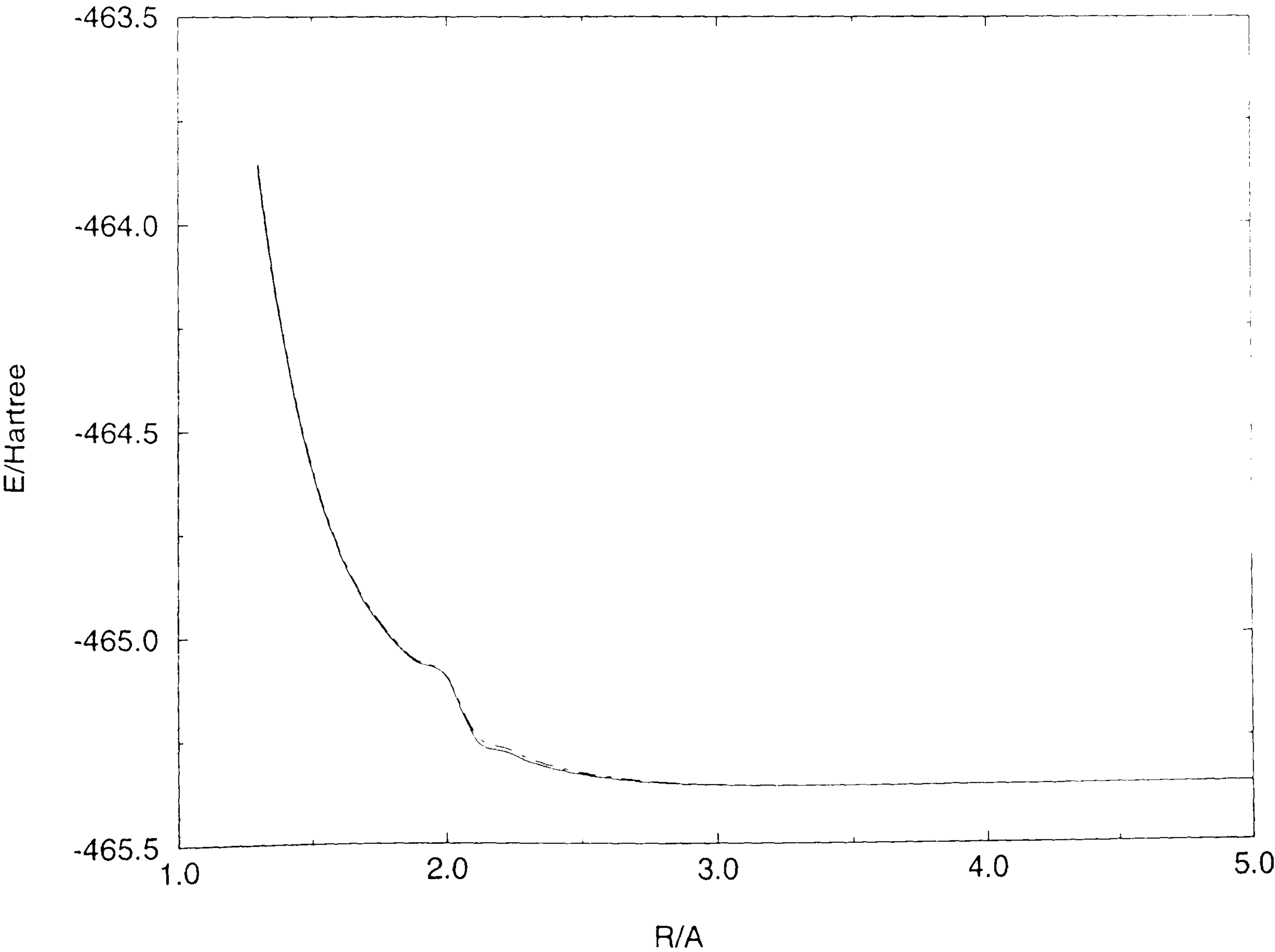
B.3.14 The CI results for the $^4\Sigma^+$ states of AsCl^+ with the VTZ basis sets

Table B.3.14 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-463.863960	-463.853637
1.4	-464.299745	-464.290636
1.5	-464.593246	-464.585073
1.6	-464.790182	-464.782887
1.7	-464.921841	-464.915382
1.8	-465.009024	-465.003356
1.9	-465.065746	-465.060832
2.0	-465.101649	-465.097285
2.1	-465.242061	-465.230788
2.2	-465.276856	-465.267355
2.3	-465.302478	-465.294568
2.4	-465.321180	-465.314659
2.5	-465.334682	-465.329349
2.6	-465.344301	-465.339968
2.7	-465.351049	-465.347544
2.8	-465.355692	-465.352866
3.0	-465.360830	-465.358997
3.5	-465.363072	-465.362414
4.0	-465.361687	-465.361406
4.5	-465.360357	-465.360215
5.0	-465.359487	-465.359406

E/Hartree

Figure B.3.14 Calculated potential energy curves



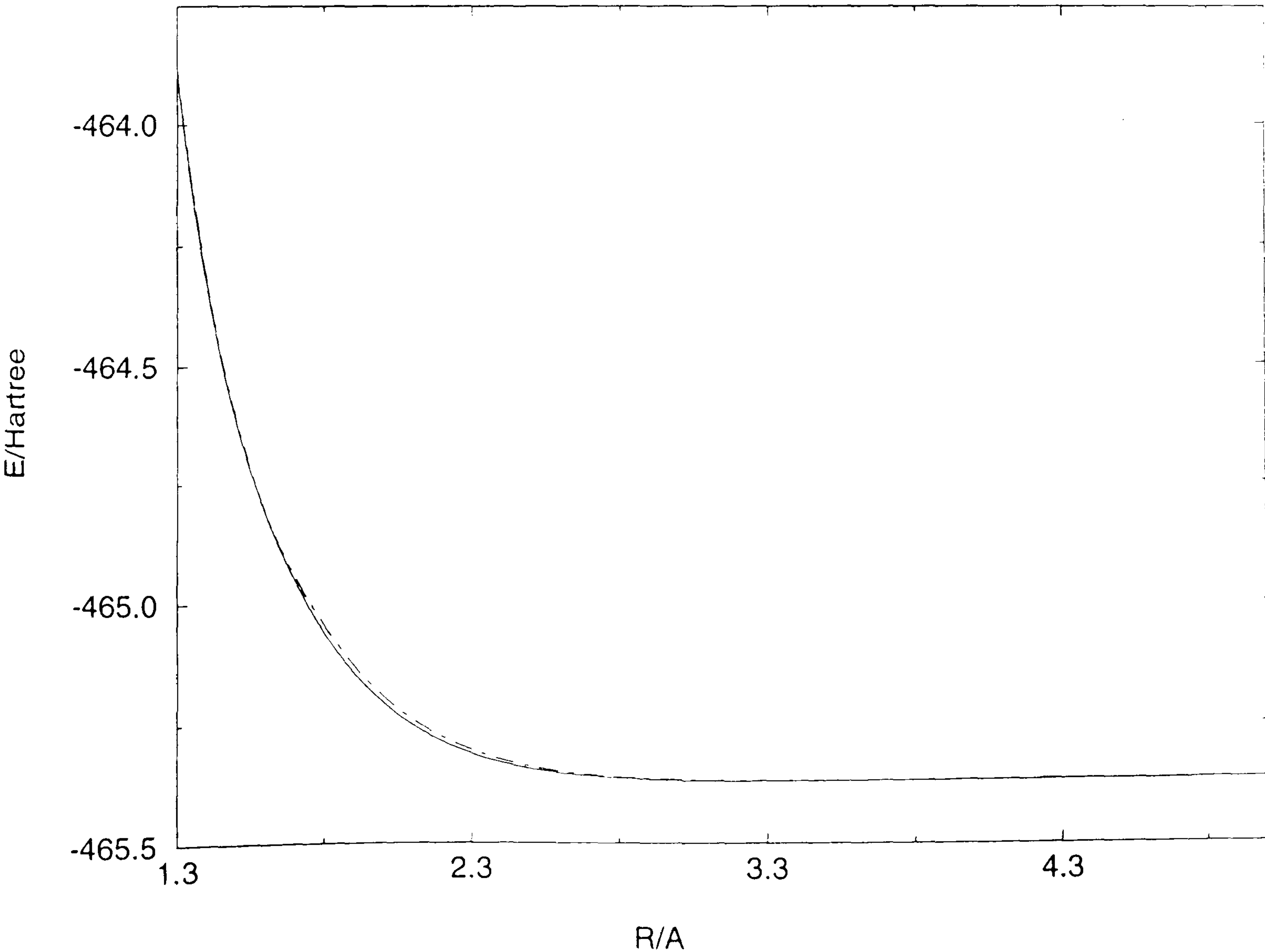
B.3.15 The CI results for the $^4\Sigma^+$ states of AsCl^+ with the VQZ basis sets

Table B.3.15 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-463.890710	-463.880488
1.4	-464.322112	-464.313503
1.5	-464.613059	-464.606043
1.6	-464.807842	-464.804411
1.7	-464.949270	-464.939959
1.8	-465.059786	-465.043853
1.9	-465.142224	-465.127201
2.0	-465.204157	-465.190971
2.1	-465.250634	-465.239354
2.2	-465.285272	-465.275777
2.3	-465.310826	-465.302930
2.4	-465.329455	-465.322951
2.5	-465.342855	-465.337538
2.6	-465.352347	-465.348028
2.7	-465.358951	-465.355457
2.8	-465.363444	-465.360625
3.0	-465.368293	-465.366460
3.5	-465.370000	-465.369338
4.0	-465.368320	-465.368037
4.5	-465.366842	-465.366698
5.0	-465.365895	-465.365813

E/Hartree

Figure B.3.15 Calculated potential energy curves



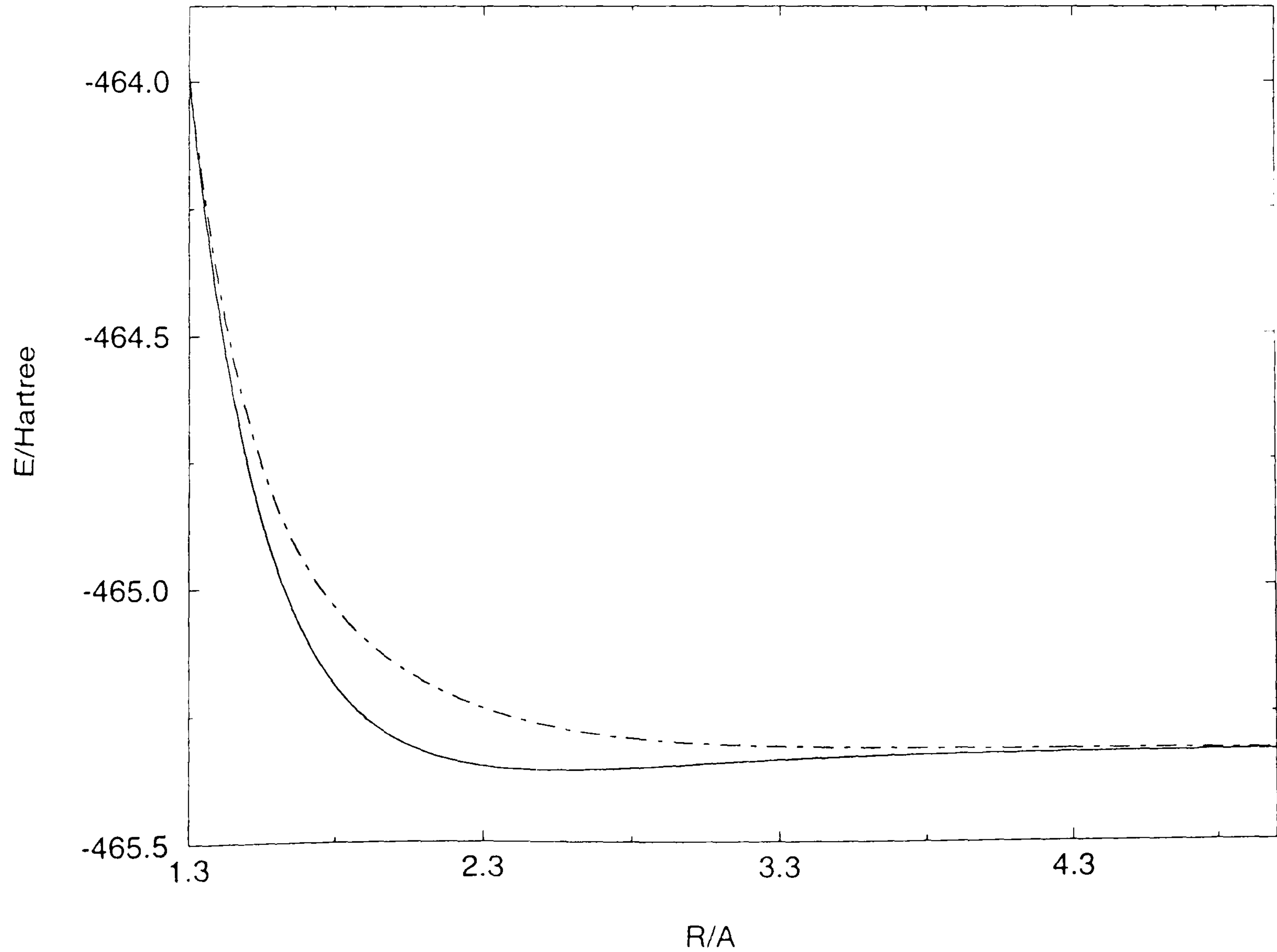
B.3.16 The CI results for the $^4\Pi$ states of AsCl^+ with the VDZ basis sets

Table B.3.16 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-463.988713	-463.982833
1.4	-464.441518	-464.390420
1.5	-464.751459	-464.657503
1.6	-464.959639	-464.834422
1.7	-465.098903	-464.954282
1.8	-465.192231	-465.038749
1.9	-465.254821	-465.100796
2.0	-465.296551	-465.147900
2.1	-465.323933	-465.184514
2.2	-465.341363	-465.213428
2.3	-465.351867	-465.236459
2.4	-465.357558	-465.254841
2.5	-465.359931	-465.269479
2.6	-465.360052	-465.281085
2.7	-465.358690	-465.290236
2.8	-465.356401	-465.297411
3.0	-465.350557	-465.307347
3.5	-465.337150	-465.317908
4.0	-465.329825	-465.320670
4.5	-465.326546	-465.321493
5.0	-465.325085	-465.321870

E/Hartree

Figure B.3.16 Calculated potential energy curves



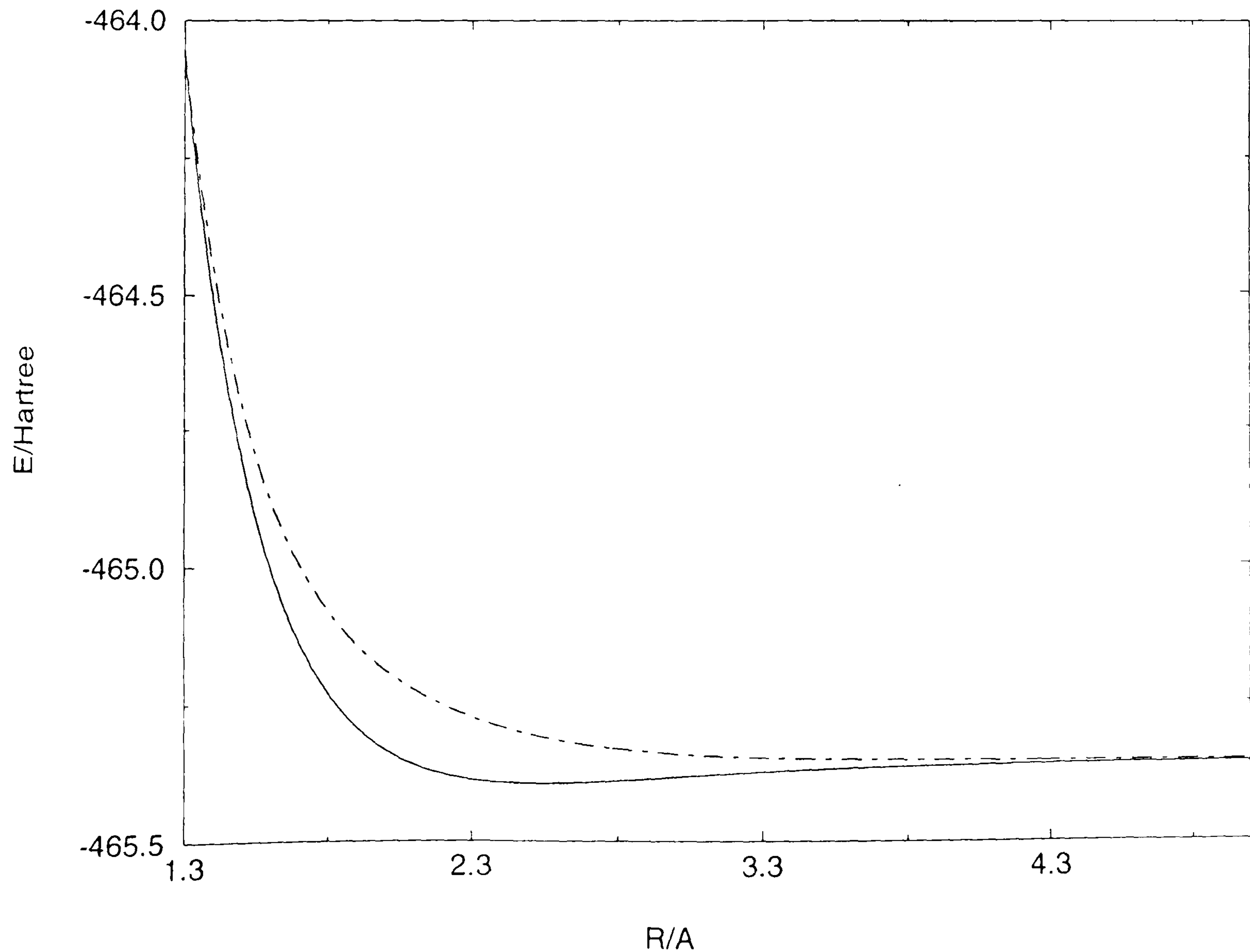
B.3.17 The CI results for the $^4\Pi$ states of AsCl^+ with the VTZ basis sets

Table B.3.17 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-464.062118	-464.052844
1.4	-464.501439	-464.442896
1.5	-464.798491	-464.700754
1.6	-464.999736	-464.874261
1.7	-465.136794	-464.994184
1.8	-465.230136	-465.079456
1.9	-465.293146	-465.141671
2.0	-465.335013	-465.188215
2.1	-465.362188	-465.223916
2.2	-465.379172	-465.251878
2.3	-465.389099	-465.274070
2.4	-465.394170	-465.291774
2.5	-465.395944	-465.305889
2.6	-465.395535	-465.317104
2.7	-465.393739	-465.325966
2.8	-465.391122	-465.332926
3.0	-465.384910	-465.342573
3.5	-465.371489	-465.352771
4.0	-465.364389	-465.355386
4.5	-465.361237	-465.356153
5.0	-465.359800	-465.356502

E/Hartree

Figure B.3.17 Calculated potential energy curves



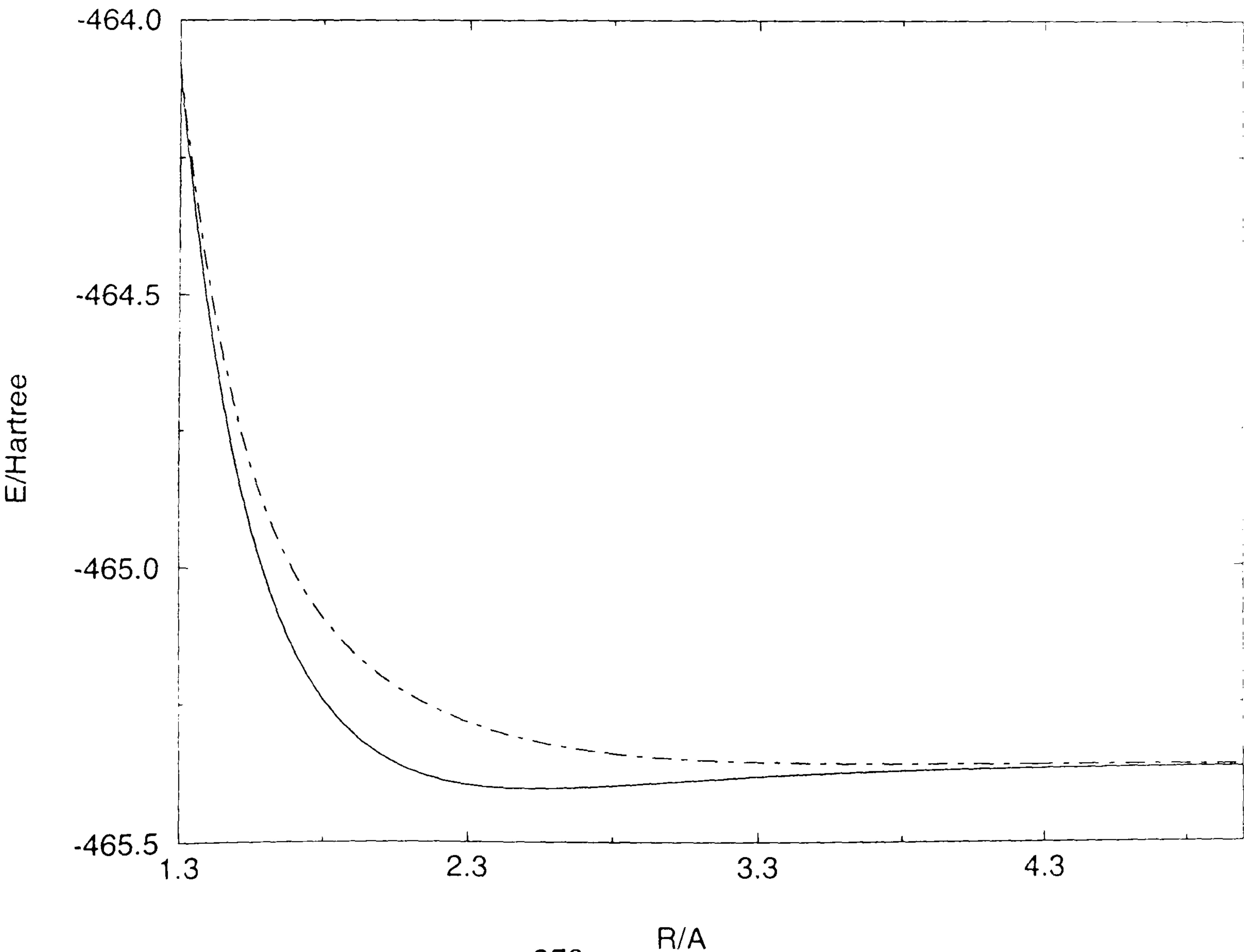
B.3.18 The CI results for the $^4\Pi$ states of AsCl^+ with the VQZ basis sets

Table B.3.18 Theoretical energy values

R/Å	ROOT1	ROOT2
1.3	-464.087523	-464.077294
1.4	-464.523208	-464.461560
1.5	-464.817931	-464.717065
1.6	-465.016300	-464.889090
1.7	-465.150004	-465.007370
1.8	-465.240407	-465.090929
1.9	-465.301562	-465.151787
2.0	-465.342638	-465.197498
2.1	-465.369683	-465.232756
2.2	-465.386809	-465.260473
2.3	-465.396926	-465.282494
2.4	-465.402135	-465.300046
2.5	-465.403971	-465.314014
2.6	-465.403550	-465.325079
2.7	-465.401682	-465.333792
2.8	-465.398953	-465.340605
3.0	-465.392461	-465.349968
3.5	-465.378464	-465.359621
4.0	-465.371054	-465.361941
4.5	-465.367739	-465.362566
5.0	-465.366215	-465.362845

E/Hartree

Figure B.3.18 Calculated potential energy curves



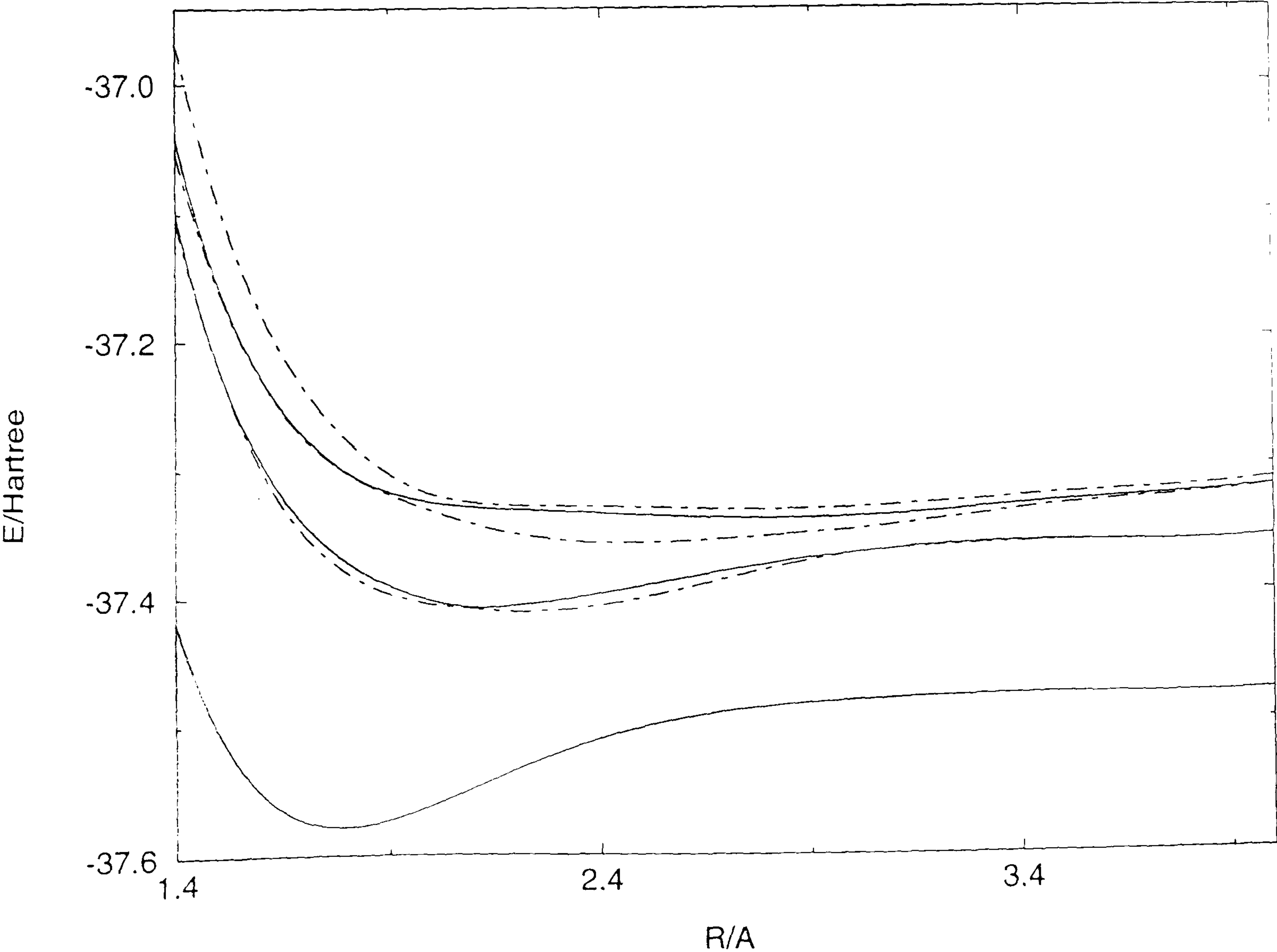
B.4.1 The CI results for the $^2\Sigma^+$ states of BBr^+ with the VDZ basis sets

Table B.4.1 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5	ROOT6
1.4	-37.417092	-37.105157	-37.097679	-37.052252	-37.040100	-36.966830
1.5	-37.504893	-37.220174	-37.219638	-37.159074	-37.155896	-37.092422
1.6	-37.552460	-37.299339	-37.293678	-37.229370	-37.228330	-37.177856
1.7	-37.573872	-37.349253	-37.341015	-37.274713	-37.272974	-37.236105
1.8	-37.578654	-37.379443	-37.371098	-37.301589	-37.301107	-37.275977
1.9	-37.573285	-37.396393	-37.390074	-37.318556	-37.316656	-37.302786
2.0	-37.562214	-37.404535	-37.401695	-37.330999	-37.324553	-37.318412
2.1	-37.548538	-37.408127	-37.406901	-37.341749	-37.328511	-37.324860
2.2	-37.534435	-37.410593	-37.405574	-37.349647	-37.330695	-37.327108
2.3	-37.521407	-37.409816	-37.401980	-37.354511	-37.332379	-37.328035
2.4	-37.510358	-37.406354	-37.397092	-37.356906	-37.334102	-37.328853
2.5	-37.501621	-37.400825	-37.391581	-37.357477	-37.335901	-37.329932
2.6	-37.495059	-37.393976	-37.385913	-37.356806	-37.337571	-37.331159
2.7	-37.490268	-37.386592	-37.380437	-37.355365	-37.338866	-37.332211
2.8	-37.486807	-37.379387	-37.375418	-37.353487	-37.339584	-37.332758
2.9	-37.484300	-37.372960	-37.371064	-37.351297	-37.339583	-37.332587
3.0	-37.482465	-37.367803	-37.367516	-37.348676	-37.338797	-37.331671
3.1	-37.481111	-37.364803	-37.364174	-37.345455	-37.337273	-37.330156
3.2	-37.480106	-37.362825	-37.361901	-37.341732	-37.335170	-37.328260
3.5	-37.478432	-37.359530	-37.359013	-37.330566	-37.327560	-37.321986
4.0	-37.477672	-37.356958	-37.356946	-37.318089	-37.317333	-37.311953

E/Hartree

Figure B.4.1 Calculated potential energy curves



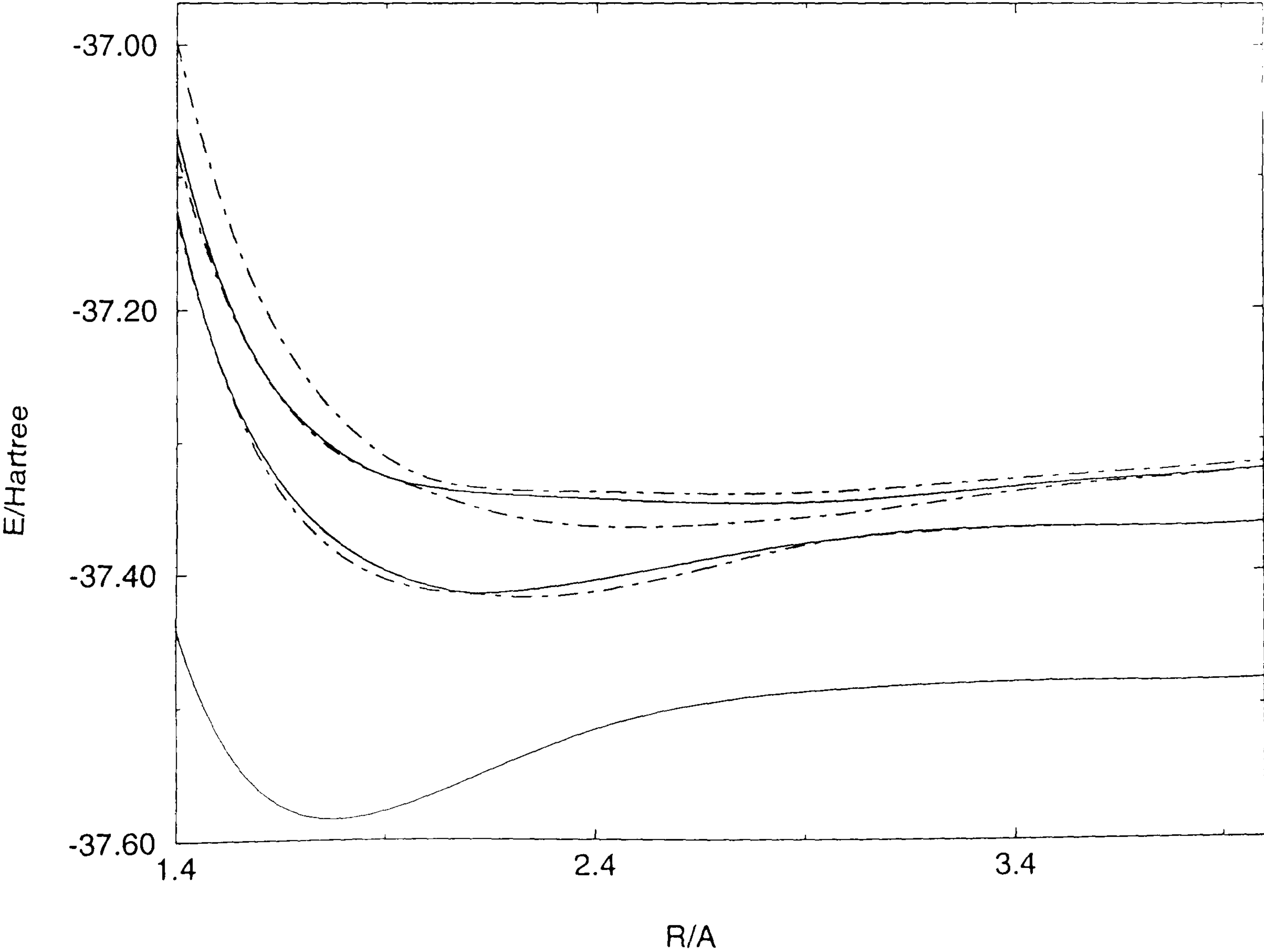
B.4.2 The CI results for the $^2\Sigma^+$ states of BBr^+ with the VTZ basis sets

Table B.4.2 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5	ROOT6
1.4	-37.441137	-37.130352	-37.123968	-37.080599	-37.066585	-36.996918
1.5	-37.520401	-37.237933	-37.236628	-37.178190	-37.174009	-37.111504
1.6	-37.562504	-37.311600	-37.305597	-37.242435	-37.241519	-37.190896
1.7	-37.580820	-37.358307	-37.350015	-37.285117	-37.282723	-37.245776
1.8	-37.584151	-37.386856	-37.378509	-37.310873	-37.309119	-37.284098
1.9	-37.578366	-37.403145	-37.396685	-37.325724	-37.325713	-37.310710
2.0	-37.567451	-37.411184	-37.407986	-37.337557	-37.333814	-37.327160
2.1	-37.554174	-37.414391	-37.413718	-37.348484	-37.338096	-37.334167
2.2	-37.540491	-37.416993	-37.412646	-37.356857	-37.340535	-37.336711
2.3	-37.527771	-37.416419	-37.409285	-37.362125	-37.342313	-37.337772
2.4	-37.516861	-37.413148	-37.404557	-37.364799	-37.343956	-37.338516
2.5	-37.508093	-37.407747	-37.399119	-37.365527	-37.345534	-37.339331
2.6	-37.501364	-37.400944	-37.393454	-37.364913	-37.346887	-37.340162
2.7	-37.496319	-37.393537	-37.387939	-37.363454	-37.347799	-37.340743
2.8	-37.492553	-37.386283	-37.382878	-37.361482	-37.348084	-37.340790
2.9	-37.489721	-37.379852	-37.378503	-37.359089	-37.347613	-37.340137
3.0	-37.487566	-37.374959	-37.374788	-37.356114	-37.346341	-37.338795
3.1	-37.485910	-37.372254	-37.371316	-37.352438	-37.344350	-37.336929
3.2	-37.484630	-37.370263	-37.369160	-37.348283	-37.341835	-37.334756
3.5	-37.482337	-37.366757	-37.366198	-37.336283	-37.333346	-37.327939
4.0	-37.481107	-37.363737	-37.363720	-37.323029	-37.322288	-37.316990

E/Hartree

Figure B.4.2 Calculated potential energy curves



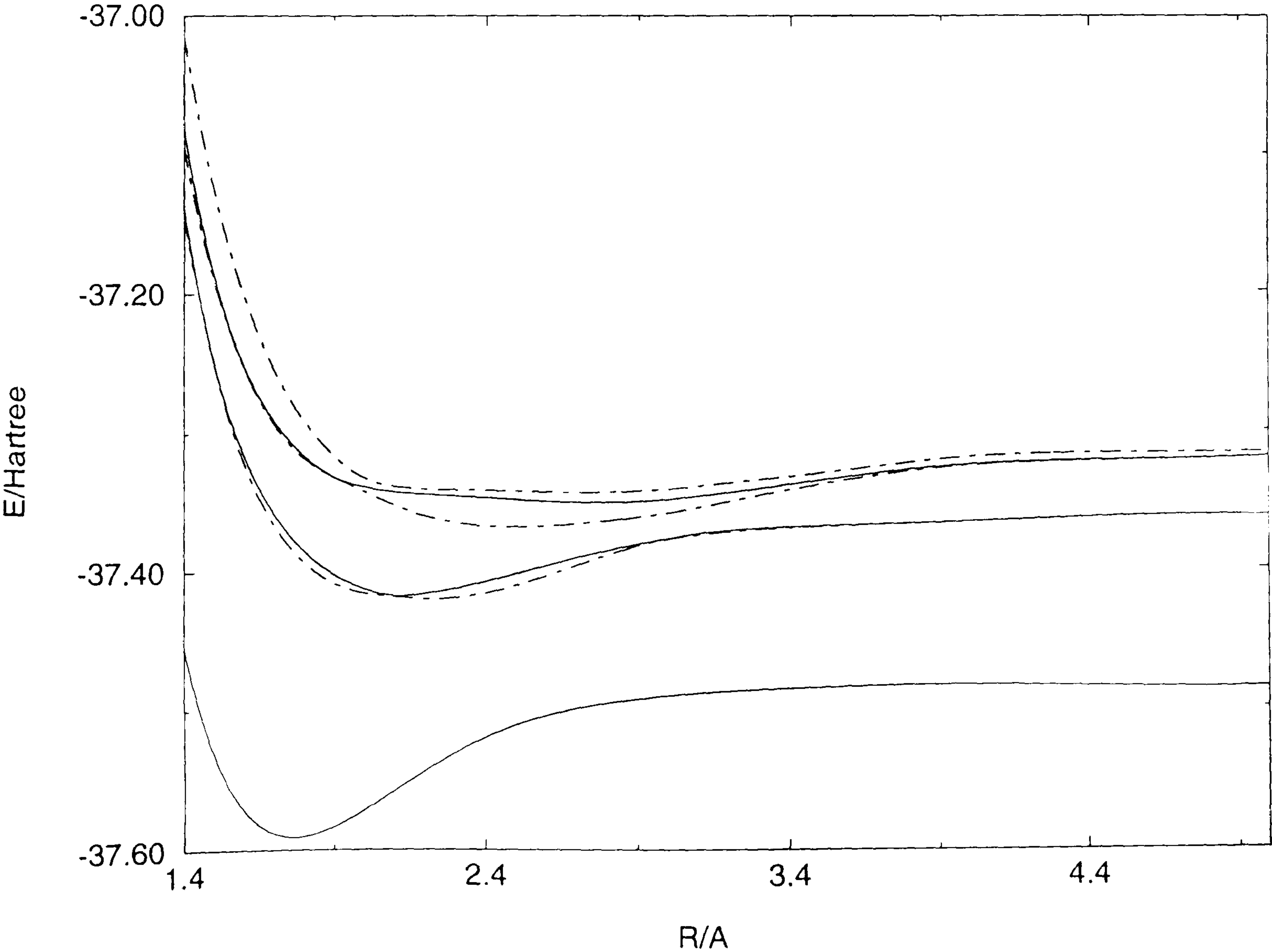
B.4.3 The CI results for the $^2\Sigma^+$ states of BBr^+ with the VQZ basis sets

Table B.4.3 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5	ROOT6
1.4	-37.454137	-37.144006	-37.137448	-37.093634	-37.080615	-37.013820
1.5	-37.531249	-37.248957	-37.248065	-37.189280	-37.185699	-37.123606
1.6	-37.571648	-37.320732	-37.315109	-37.252222	-37.251039	-37.200817
1.7	-37.588472	-37.365869	-37.357845	-37.293273	-37.290797	-37.254008
1.8	-37.590454	-37.393077	-37.384897	-37.317634	-37.315853	-37.290889
1.9	-37.583480	-37.408236	-37.401874	-37.331314	-37.331233	-37.316301
2.0	-37.571576	-37.415352	-37.412204	-37.341927	-37.338495	-37.331892
2.1	-37.557541	-37.417852	-37.417177	-37.352014	-37.342096	-37.338221
2.2	-37.543340	-37.419898	-37.415604	-37.359864	-37.344076	-37.340251
2.3	-37.530317	-37.418954	-37.411929	-37.364838	-37.345578	-37.340995
2.4	-37.519276	-37.415476	-37.407041	-37.367390	-37.347075	-37.341571
2.5	-37.510495	-37.409998	-37.401553	-37.368116	-37.348582	-37.342305
2.6	-37.503819	-37.403203	-37.395908	-37.367571	-37.349894	-37.343087
2.7	-37.498852	-37.395852	-37.390454	-37.366209	-37.350767	-37.343620
2.8	-37.495166	-37.388679	-37.385471	-37.364323	-37.350999	-37.343614
2.9	-37.492397	-37.382345	-37.381179	-37.361963	-37.350454	-37.342908
3.0	-37.490281	-37.377708	-37.377395	-37.358945	-37.349093	-37.341521
3.1	-37.488637	-37.375053	-37.374028	-37.355174	-37.347011	-37.339620
3.2	-37.487345	-37.373084	-37.371934	-37.350918	-37.344411	-37.337416
3.5	-37.484914	-37.369485	-37.368917	-37.338682	-37.335714	-37.330470
4.0	-37.483361	-37.366137	-37.366118	-37.325066	-37.324323	-37.319032
4.5	-37.484967	-37.362563	-37.362480	-37.321611	-37.321381	-37.316202
5.0	-37.485339	-37.362296	-37.362224	-37.319412	-37.319306	-37.315723

E/Hartree

Figure B.4.3 Calculated potential energy curves



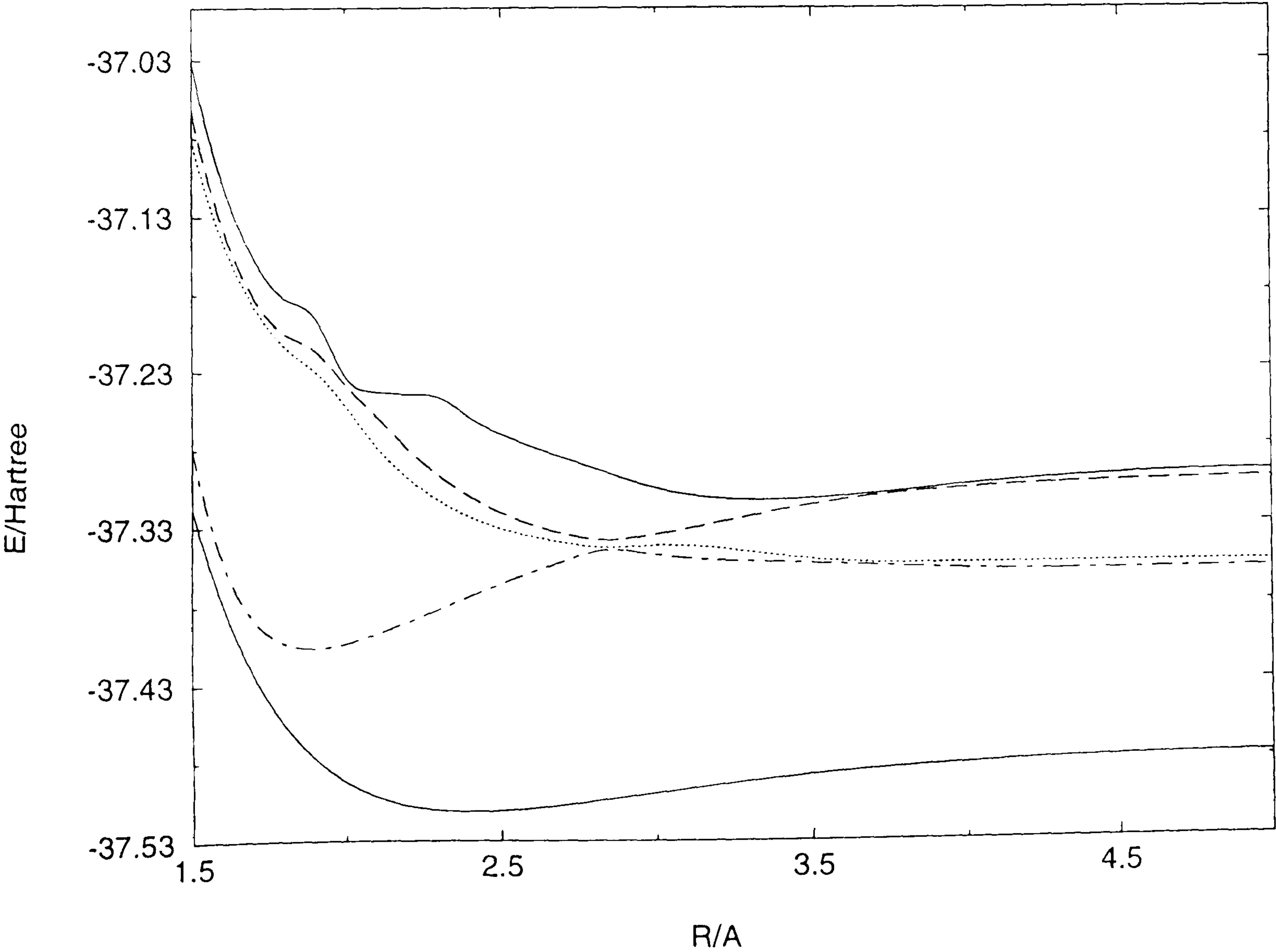
B.4.4 The CI results for the $^2\Pi$ states of BBr^+ with the VDZ basis sets

Table B.4.4 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-37.320469	-37.282005	-37.084055	-37.065660	-37.033682
1.6	-37.382105	-37.354862	-37.148788	-37.139627	-37.111565
1.7	-37.426822	-37.391803	-37.189884	-37.184530	-37.158882
1.8	-37.459372	-37.406717	-37.216746	-37.208389	-37.185534
1.9	-37.481647	-37.410056	-37.233326	-37.219800	-37.198409
2.0	-37.496402	-37.406973	-37.255660	-37.242105	-37.236907
2.1	-37.505787	-37.400879	-37.281927	-37.262267	-37.246619
2.2	-37.511342	-37.393317	-37.301803	-37.283330	-37.248273
2.3	-37.514159	-37.385270	-37.316470	-37.300312	-37.250498
2.4	-37.515026	-37.377157	-37.327070	-37.313929	-37.263528
2.5	-37.514521	-37.369418	-37.334553	-37.324501	-37.274237
2.6	-37.513082	-37.362280	-37.339834	-37.332497	-37.282474
2.7	-37.511042	-37.355717	-37.343748	-37.338249	-37.289591
2.8	-37.508665	-37.349951	-37.346837	-37.341965	-37.296490
3.0	-37.503627	-37.352208	-37.346327	-37.339124	-37.309655
3.5	-37.492510	-37.358143	-37.355663	-37.320664	-37.316743
4.0	-37.485854	-37.362333	-37.358435	-37.310655	-37.308426
4.5	-37.482549	-37.363329	-37.358595	-37.306905	-37.302315
5.0	-37.480969	-37.362770	-37.358541	-37.304921	-37.300520

E/Hartree

Figure B.4.4 Calculated potential energy curves



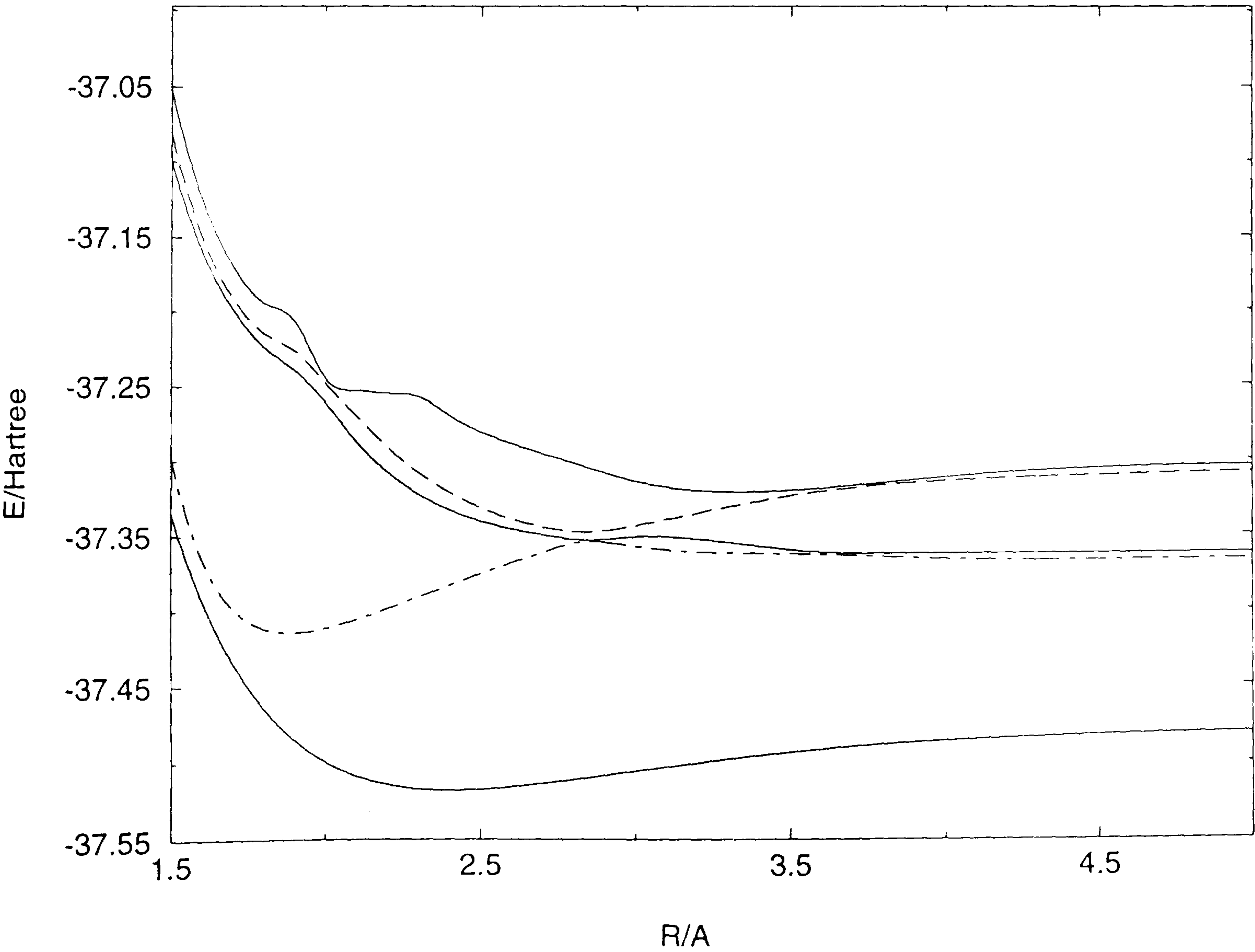
B.4.5 The CI results for the $^2\Pi$ states of BBr^+ with the VTZ basis sets

Table B.4.5 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-37.337610	-37.300513	-37.101668	-37.083567	-37.054276
1.6	-37.394632	-37.366997	-37.162235	-37.152359	-37.127231
1.7	-37.436352	-37.400520	-37.201401	-37.194062	-37.171831
1.8	-37.466943	-37.414034	-37.226494	-37.217403	-37.197208
1.9	-37.488197	-37.416931	-37.242101	-37.229306	-37.209670
2.0	-37.5025600	-37.413825	-37.263391	-37.250582	-37.247294
2.1	-37.511834	-37.407989	-37.289823	-37.272462	-37.255322
2.2	-37.517415	-37.400726	-37.309850	-37.293353	-37.257228
2.3	-37.520280	-37.392927	-37.324588	-37.310136	-37.259563
2.4	-37.521146	-37.384977	-37.335178	-37.323500	-37.272541
2.5	-37.520559	-37.377237	-37.342607	-37.333794	-37.283459
2.6	-37.518976	-37.370042	-37.347862	-37.341398	-37.291426
2.7	-37.516740	-37.363348	-37.351850	-37.346647	-37.298197
2.8	-37.514138	-37.357450	-37.354975	-37.349868	-37.304681
3.0	-37.508636	-37.360157	-37.353773	-37.346130	-37.317032
3.5	-37.496547	-37.365394	-37.362796	-37.326834	-37.323219
4.0	-37.489314	-37.369233	-37.365230	-37.317269	-37.314717
4.5	-37.485728	-37.370033	-37.365215	-37.313553	-37.308783
5.0	-37.484024	-37.369381	-37.365078	-37.311509	-37.307032

E/Hartree

Figure B.4.5 Calculated potential energy curves



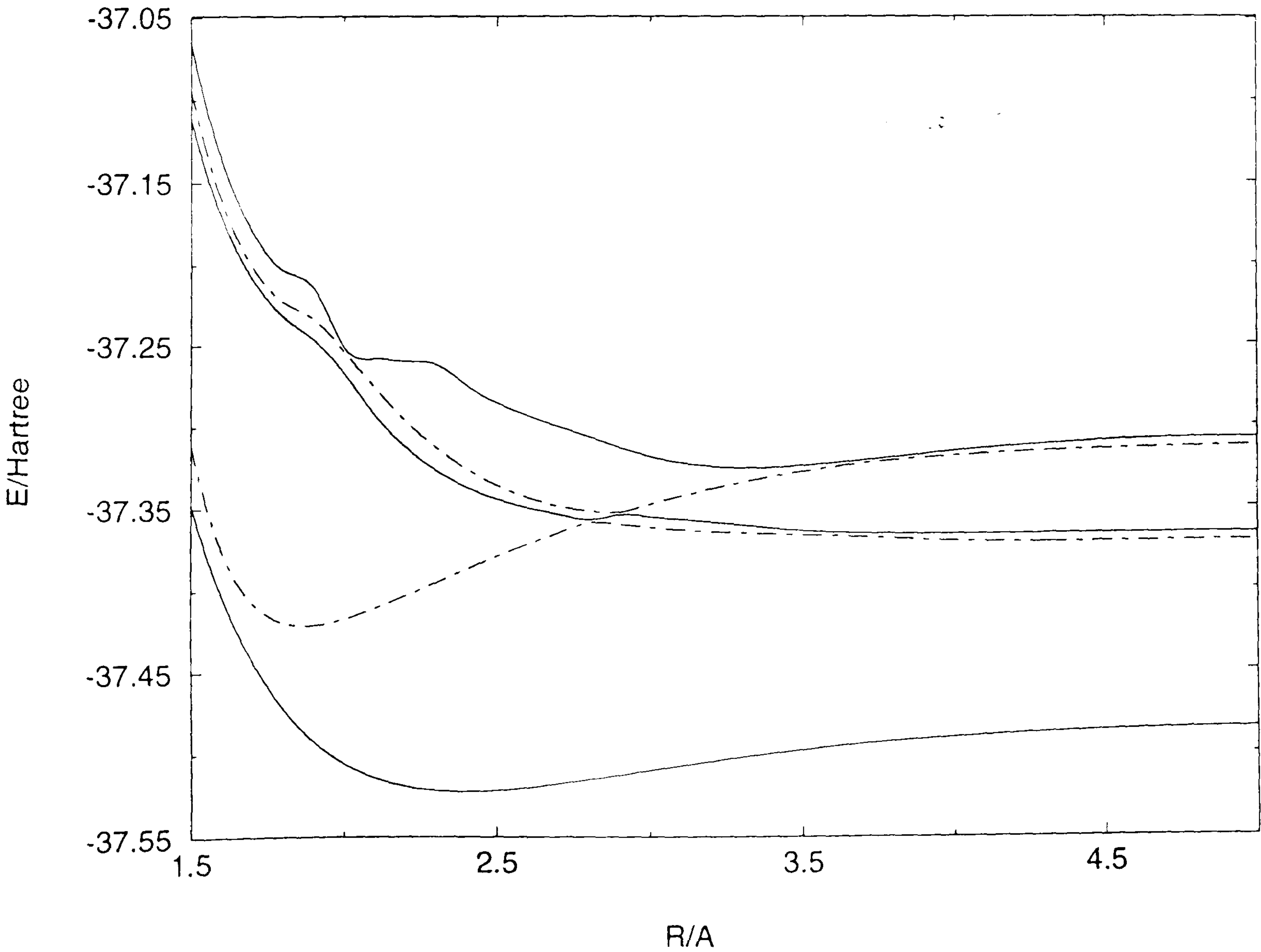
B.4.6 The CI results for the $^2\Pi$ states of BBr^+ with the VQZ basis sets

Table B.4.6 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-37.348369	-37.311604	-37.112399	-37.094717	-37.065718
1.6	-37.403779	-37.376204	-37.171456	-37.161573	-37.136860
1.7	-37.444082	-37.408146	-37.209224	-37.201655	-37.179939
1.8	-37.473368	-37.420357	-37.232912	-37.223795	-37.204016
1.9	-37.493501	-37.422154	-37.247309	-37.234729	-37.215382
2.0	-37.506965	-37.418122	-37.267942	-37.254819	-37.252043
2.1	-37.515529	-37.411593	-37.293542	-37.276614	-37.258879
2.2	-37.520599	-37.403834	-37.313053	-37.297080	-37.260342
2.3	-37.523133	-37.395711	-37.327511	-37.313597	-37.262526
2.4	-37.523815	-37.387578	-37.337985	-37.326810	-37.275683
2.5	-37.523150	-37.379754	-37.345396	-37.337021	-37.286640
2.6	-37.521554	-37.372555	-37.350705	-37.344551	-37.294564
2.7	-37.519340	-37.365897	-37.354804	-37.349697	-37.301282
2.8	-37.516768	-37.360114	-37.357965	-37.352823	-37.307682
2.9	-37.514076	-37.361170	-37.355403	-37.353518	-37.314293
3.0	-37.511313	-37.363213	-37.356694	-37.348787	-37.319888
3.1	-37.508569	-37.364810	-37.358357	-37.344095	-37.323847
3.2	-37.505936	-37.365991	-37.360212	-37.339805	-37.326135
3.5	-37.499091	-37.368196	-37.365578	-37.329321	-37.325739
4.0	-37.491574	-37.371857	-37.367614	-37.319851	-37.317011
4.5	-37.487754	-37.372442	-37.367389	-37.315992	-37.310939
5.0	-37.485925	-37.371616	-37.367141	-37.313758	-37.309098

E/Hartree

Figure B.4.6 Calculated potential energy curves



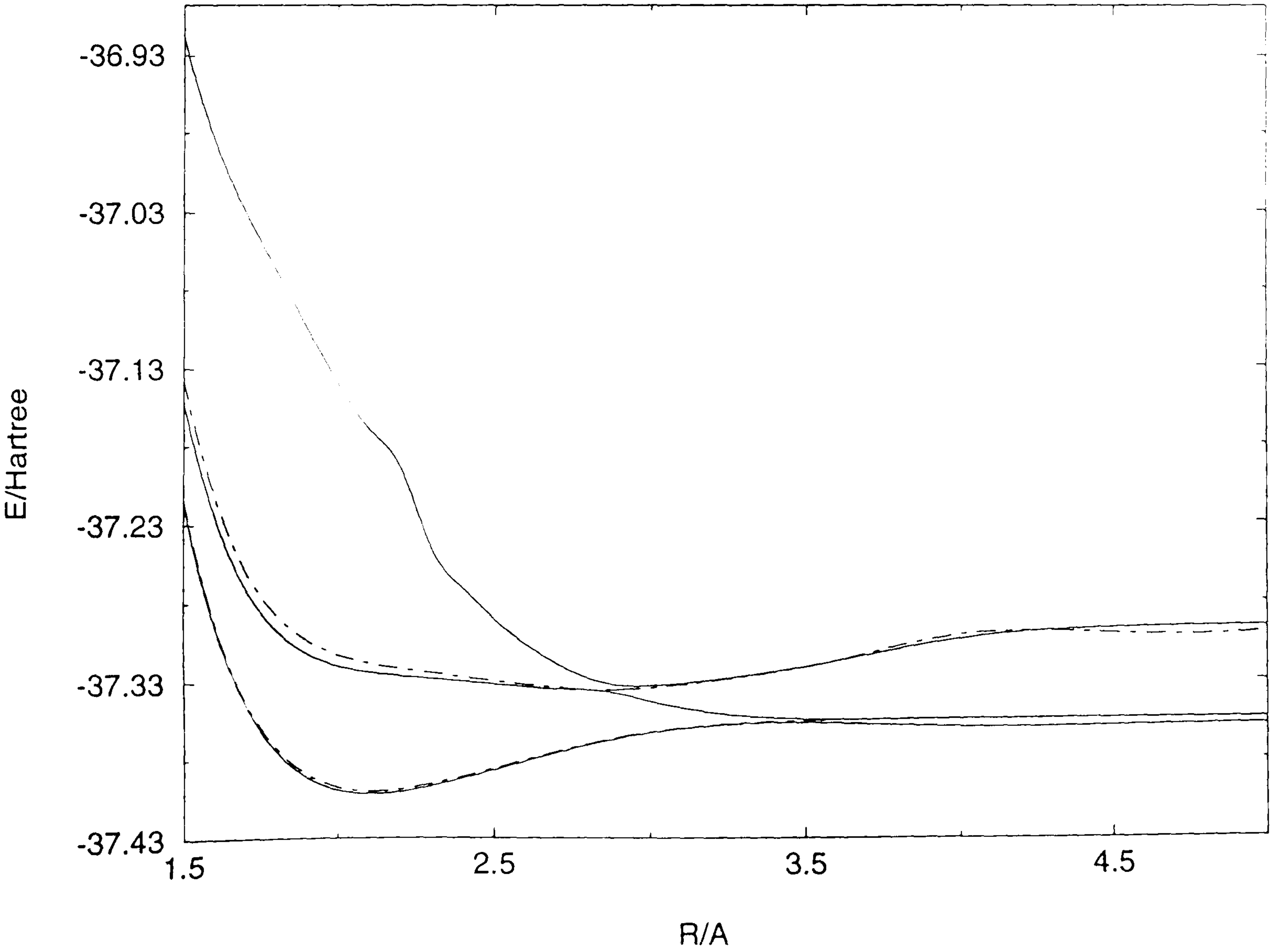
B.4.7 The CI results for the $^2\Sigma^-$ states of BBr^+ with the VDZ basis sets

Table B.4.7 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-37.220060	-37.217436	-37.155476	-37.140862	-36.922013
1.6	-37.299267	-37.296728	-37.228995	-37.215918	-36.988839
1.7	-37.349206	-37.346763	-37.274447	-37.262940	-37.033591
1.8	-37.379331	-37.376994	-37.301519	-37.291548	-37.070863
1.9	-37.396280	-37.394068	-37.316637	-37.308153	-37.108226
2.0	-37.404437	-37.402365	-37.324605	-37.317511	-37.143534
2.1	-37.406820	-37.404900	-37.328643	-37.322819	-37.173483
2.2	-37.405509	-37.403746	-37.330909	-37.326217	-37.198064
2.3	-37.401798	-37.400215	-37.332608	-37.328943	-37.250061
2.4	-37.396909	-37.395481	-37.334398	-37.331545	-37.275064
2.5	-37.391396	-37.390116	-37.336252	-37.334065	-37.295078
2.6	-37.385738	-37.384596	-37.337958	-37.336335	-37.310933
2.7	-37.380283	-37.379269	-37.339257	-37.338181	-37.323321
2.8	-37.375316	-37.374420	-37.339936	-37.339704	-37.332601
2.9	-37.371053	-37.370268	-37.342721	-37.339840	-37.337355
3.0	-37.367634	-37.366961	-37.347678	-37.338902	-37.337526
3.1	-37.365076	-37.364527	-37.351914	-37.337176	-37.336186
3.2	-37.363265	-37.362872	-37.355155	-37.334841	-37.334077
3.5	-37.361847	-37.360528	-37.359371	-37.326227	-37.325875
4.0	-37.364231	-37.359564	-37.359193	-37.305996	-37.308505
4.5	-37.363704	-37.359109	-37.358922	-37.305340	-37.301828
5.0	-37.362743	-37.358943	-37.358839	-37.304294	-37.300548

E/Hartree

Figure B.4.7 Calculated potential energy curves



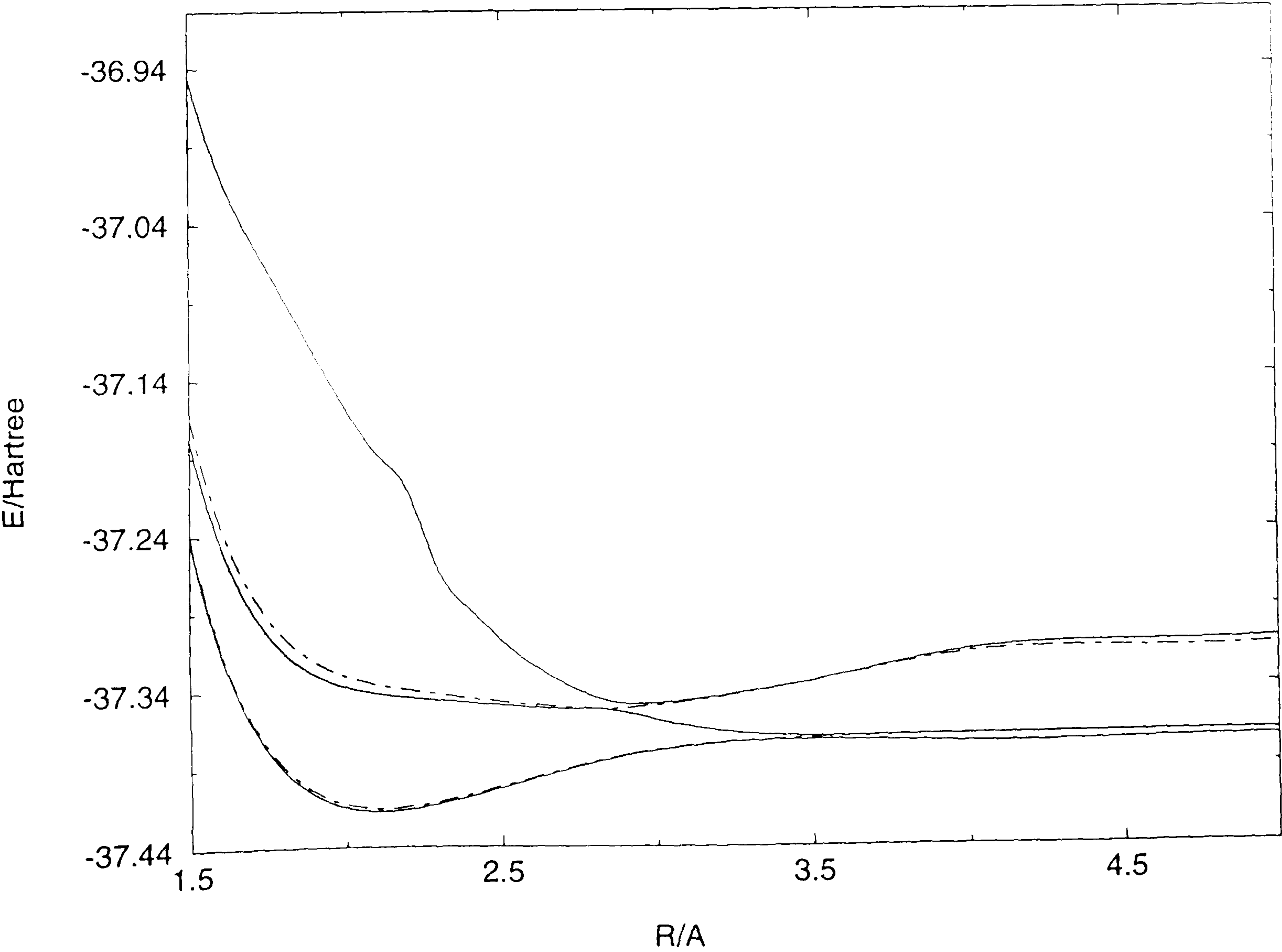
B.4.8 The CI results for the $^2\Sigma^-$ states of BBr^+ with the VTZ basis sets

Table B.4.8 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-37.237804	-37.235088	-37.173536	-37.159219	-36.941512
1.6	-37.311524	-37.308924	-37.242020	-37.229171	-37.004070
1.7	-37.358257	-37.355778	-37.284828	-37.273467	-37.046229
1.8	-37.386723	-37.384366	-37.310793	-37.300889	-37.081810
1.9	-37.403015	-37.400794	-37.325679	-37.317200	-37.118212
2.0	-37.411074	-37.409002	-37.333854	-37.326722	-37.153124
2.1	-37.413630	-37.411715	-37.338220	-37.332333	-37.183028
2.2	-37.412579	-37.410825	-37.340747	-37.335980	-37.207648
2.3	-37.409070	-37.407501	-37.342541	-37.338804	-37.260086
2.4	-37.404347	-37.402935	-37.344256	-37.341340	-37.284897
2.5	-37.398915	-37.397650	-37.345892	-37.343655	-37.304644
2.6	-37.393266	-37.392138	-37.347282	-37.345622	-37.320193
2.7	-37.387785	-37.386782	-37.348193	-37.347096	-37.332264
2.8	-37.382790	-37.381903	-37.348429	-37.348215	-37.341213
2.9	-37.378524	-37.377748	-37.351007	-37.347850	-37.345440
3.0	-37.375130	-37.374466	-37.355776	-37.346417	-37.345062
3.1	-37.372596	-37.372059	-37.359811	-37.344226	-37.343246
3.2	-37.370779	-37.370404	-37.362871	-37.341491	-37.340730
3.5	-37.369195	-37.367845	-37.366676	-37.332163	-37.331786
4.0	-37.371193	-37.366493	-37.366123	-37.314621	-37.312915
4.5	-37.370403	-37.365815	-37.365626	-37.312027	-37.308296
5.0	-37.369322	-37.365545	-37.365439	-37.310857	-37.307069

E/Hartree

Figure B.4.8 Calculated potential energy curves



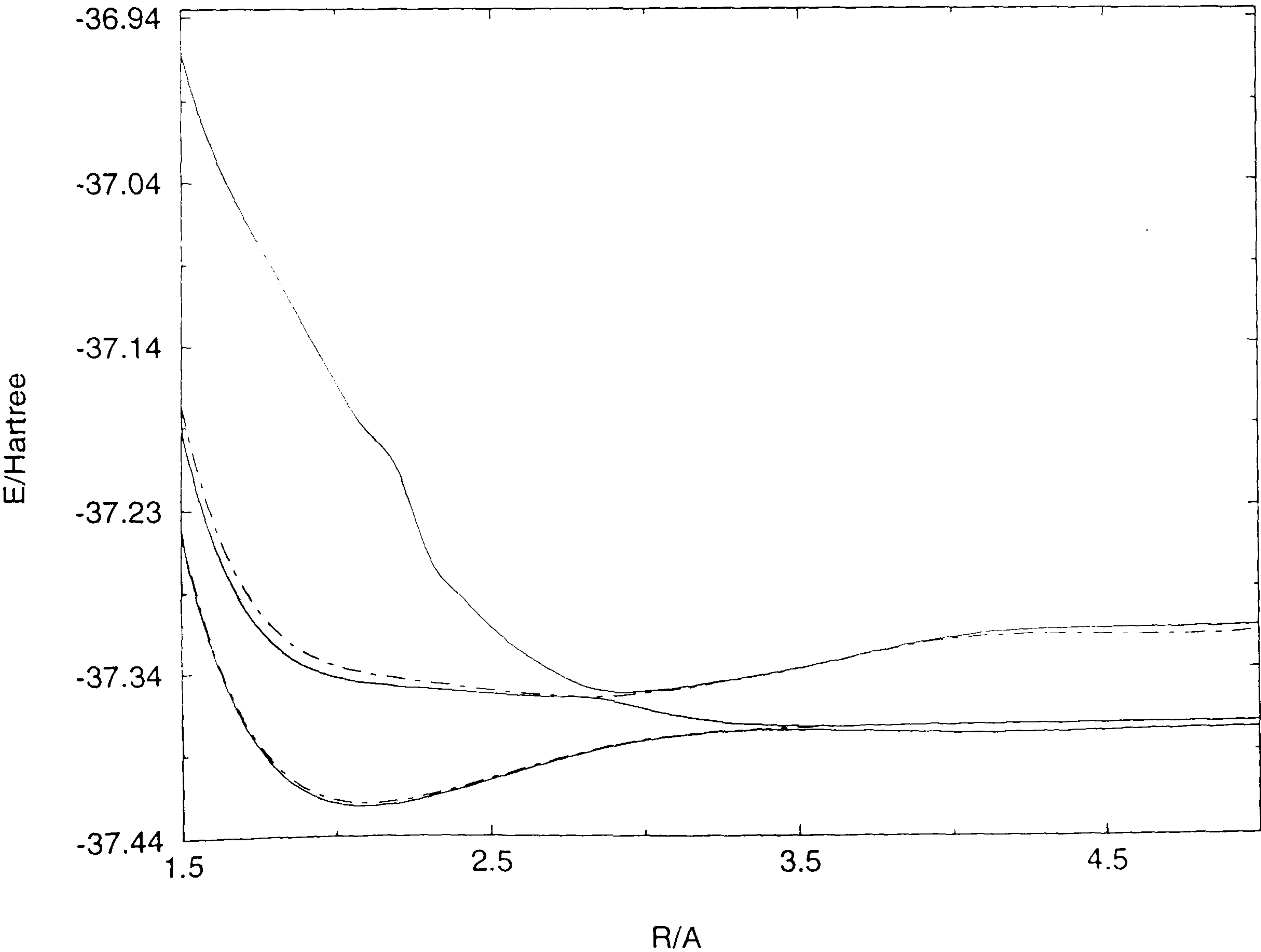
B.4.9 The CI results for the $^2\Sigma^-$ states of BBr^+ with the VQZ basis sets

Table B.4.9 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-37.248829	-37.246139	-37.185194	-37.170898	-36.955096
1.6	-37.320662	-37.318086	-37.251782	-37.238960	-37.014111
1.7	-37.365827	-37.363365	-37.292970	-37.281644	-37.054430
1.8	-37.392945	-37.390599	-37.317553	-37.307685	-37.088410
1.9	-37.408105	-37.405890	-37.331278	-37.322831	-37.123657
2.0	-37.415243	-37.413174	-37.338535	-37.331424	-37.157668
2.1	-37.417090	-37.415177	-37.342223	-37.336343	-37.186891
2.2	-37.415539	-37.413785	-37.344291	-37.339521	-37.211044
2.3	-37.411710	-37.410143	-37.345805	-37.342057	-37.263529
2.4	-37.406827	-37.405415	-37.347375	-37.344444	-37.288200
2.5	-37.401345	-37.400080	-37.348941	-37.346688	-37.307897
2.6	-37.395719	-37.394590	-37.350290	-37.348616	-37.323437
2.7	-37.390301	-37.389298	-37.351161	-37.350060	-37.335506
2.8	-37.385390	-37.384502	-37.351339	-37.351179	-37.344401
2.9	-37.381213	-37.380435	-37.354163	-37.350681	-37.348344
3.0	-37.377899	-37.377235	-37.358966	-37.349158	-37.347809
3.1	-37.375420	-37.374887	-37.362957	-37.346875	-37.345894
3.2	-37.373625	-37.373265	-37.365953	-37.344058	-37.343294
3.5	-37.372099	-37.370606	-37.369444	-37.334553	-37.334170
4.0	-37.373835	-37.368949	-37.368573	-37.316945	-37.315537
4.5	-37.372785	-37.368030	-37.367838	-37.314424	-37.310471
5.0	-37.371520	-37.367633	-37.367525	-37.313059	-37.309143

E/Hartree

Figure B.4.9 Calculated potential energy curves



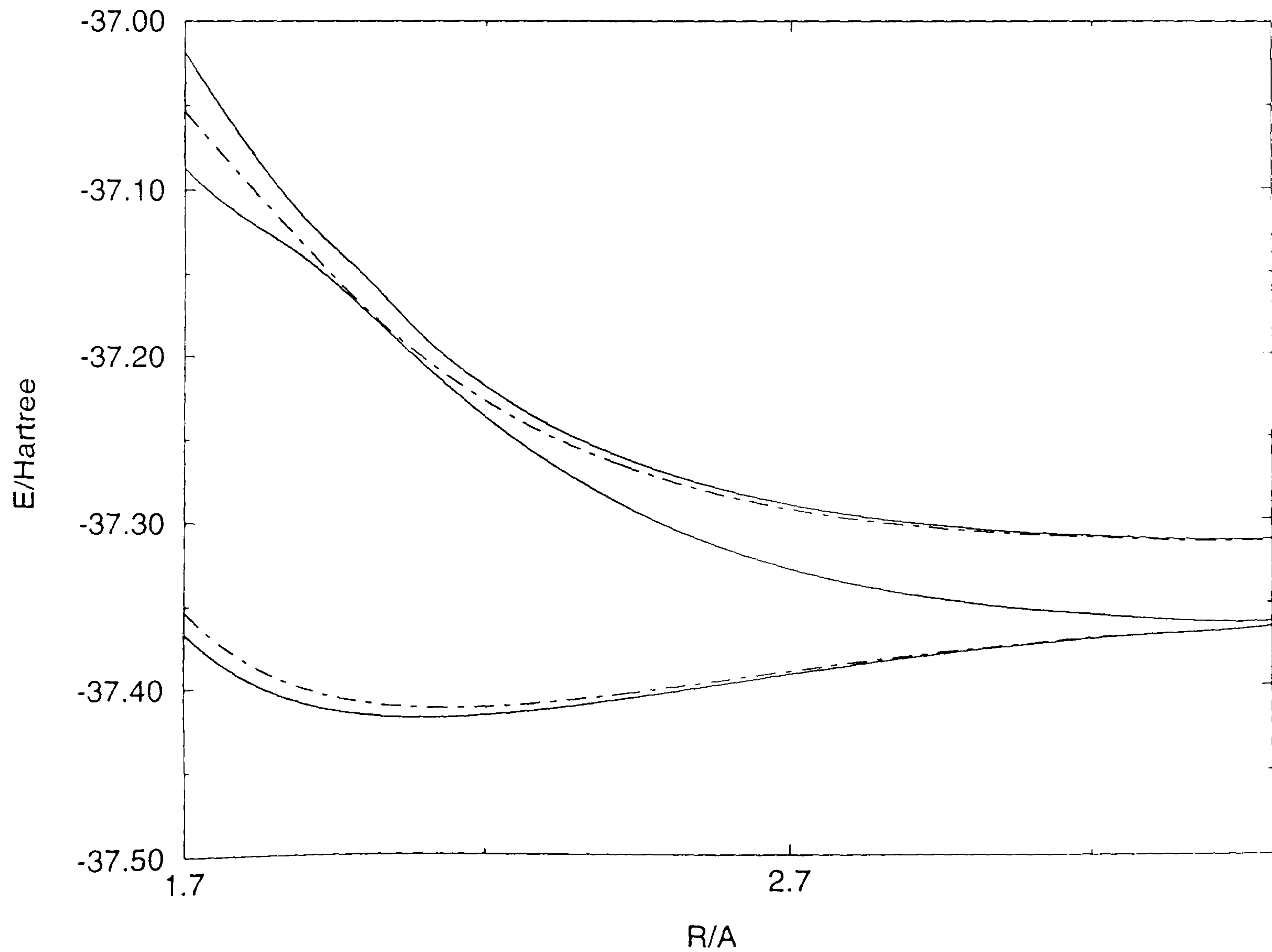
B.4.10 The CI results for the $^4\Sigma^-$ states of BBr^+ with the VDZ basis sets

Table B.4.10 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.7	-37.366241	-37.353059	-37.086991	-37.052961	-37.017804
1.8	-37.394223	-37.383217	-37.116574	-37.094084	-37.071437
1.9	-37.409554	-37.400459	-37.140665	-37.133175	-37.116800
2.0	-37.416548	-37.409067	-37.172177	-37.170770	-37.151707
2.1	-37.418274	-37.412131	-37.205969	-37.201977	-37.189398
2.2	-37.416676	-37.411651	-37.236772	-37.227154	-37.218518
2.3	-37.413073	-37.408967	-37.263443	-37.247309	-37.240871
2.4	-37.408359	-37.405001	-37.285614	-37.263322	-37.258266
2.5	-37.403125	-37.400373	-37.303607	-37.275952	-37.271877
2.6	-37.397758	-37.395494	-37.317987	-37.285837	-37.282512
2.7	-37.392506	-37.390636	-37.329340	-37.293505	-37.290776
2.8	-37.387529	-37.385977	-37.338206	-37.299388	-37.297141
2.9	-37.382922	-37.381629	-37.345050	-37.303828	-37.301975
3.0	-37.378749	-37.377674	-37.350273	-37.307111	-37.305587
3.1	-37.375038	-37.374140	-37.354202	-37.309451	-37.308167
3.2	-37.371800	-37.371062	-37.357103	-37.311076	-37.310007
3.5	-37.364593	-37.364420	-37.361394	-37.312855	-37.312226

E/Hartree

Figure B.4.10 Calculated potential energy curves



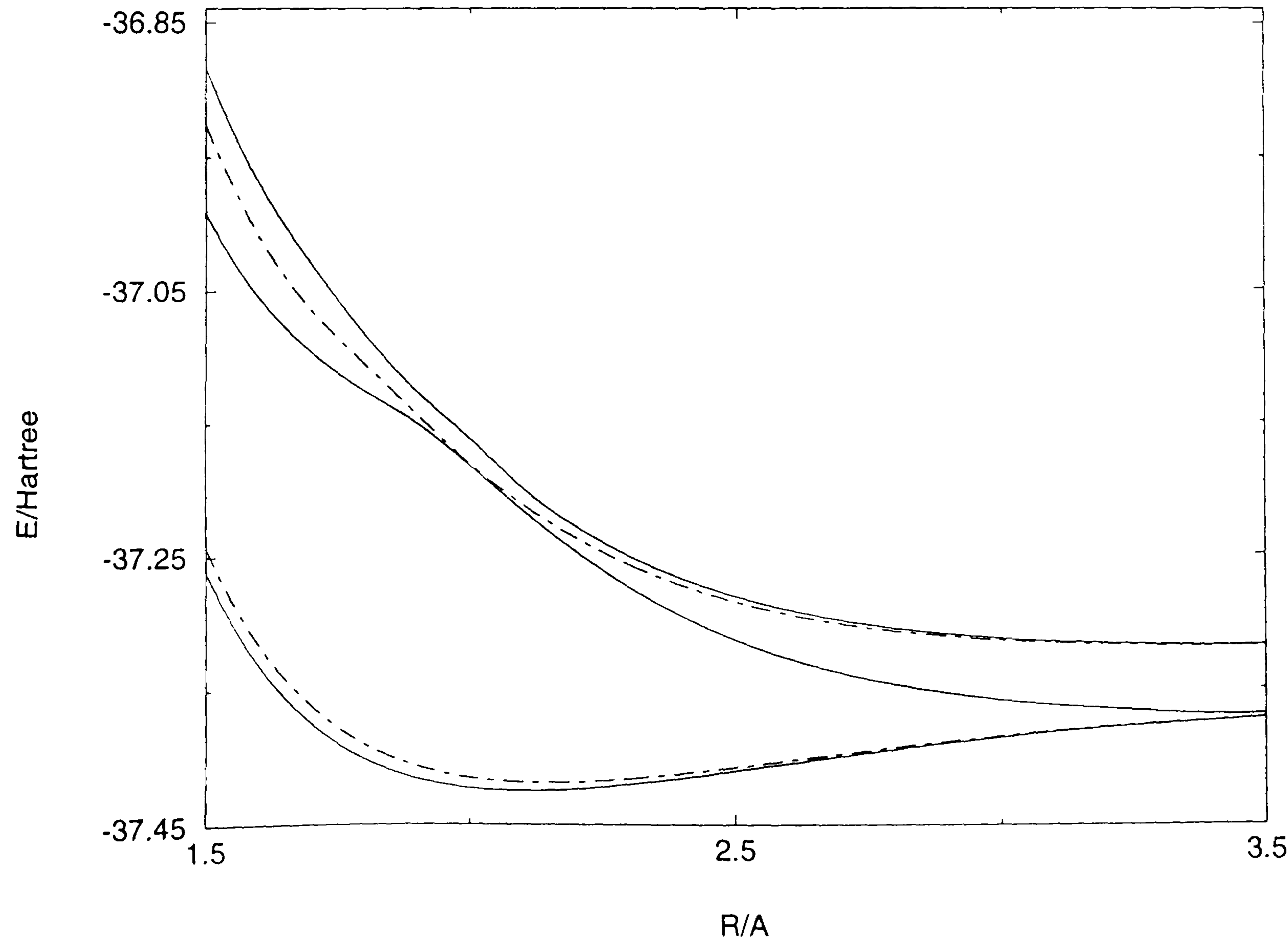
B.4.11 The CI results for the $^4\Sigma^-$ states of BBr^+ with the VTZ basis sets

Table B.4.11 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.5	-37.260538	-37.242470	-36.991236	-36.925393	-36.881947
1.6	-37.330989	-37.315450	-37.054130	-37.007417	-36.967944
1.7	-37.375080	-37.361908	-37.095728	-37.064107	-37.029122
1.8	-37.401612	-37.390582	-37.124574	-37.104115	-37.081889
1.9	-37.416402	-37.407247	-37.149117	-37.142696	-37.125514
2.0	-37.423337	-37.415803	-37.181464	-37.180036	-37.160837
2.1	-37.425262	-37.419065	-37.215603	-37.211210	-37.198889
2.2	-37.423910	-37.418834	-37.246783	-37.236461	-37.227941
2.3	-37.420522	-37.416370	-37.273586	-37.256637	-37.250213
2.4	-37.415948	-37.412551	-37.295670	-37.272581	-37.267490
2.5	-37.410768	-37.407985	-37.313436	-37.285041	-37.280912
2.6	-37.405352	-37.403061	-37.327577	-37.294668	-37.291279
2.7	-37.400060	-37.398172	-37.338612	-37.301980	-37.299193
2.8	-37.395020	-37.393458	-37.347161	-37.307467	-37.305170
2.9	-37.390348	-37.389053	-37.353718	-37.311499	-37.309605
3.0	-37.386113	-37.385038	-37.358688	-37.314366	-37.312806
3.1	-37.382359	-37.381469	-37.362412	-37.316336	-37.315046
3.2	-37.379078	-37.378353	-37.365144	-37.317573	-37.316513
3.5	-37.371852	-37.371759	-37.369092	-37.318451	-37.317816

E/Hartree

Figure B.4.11 Calculated potential energy curves



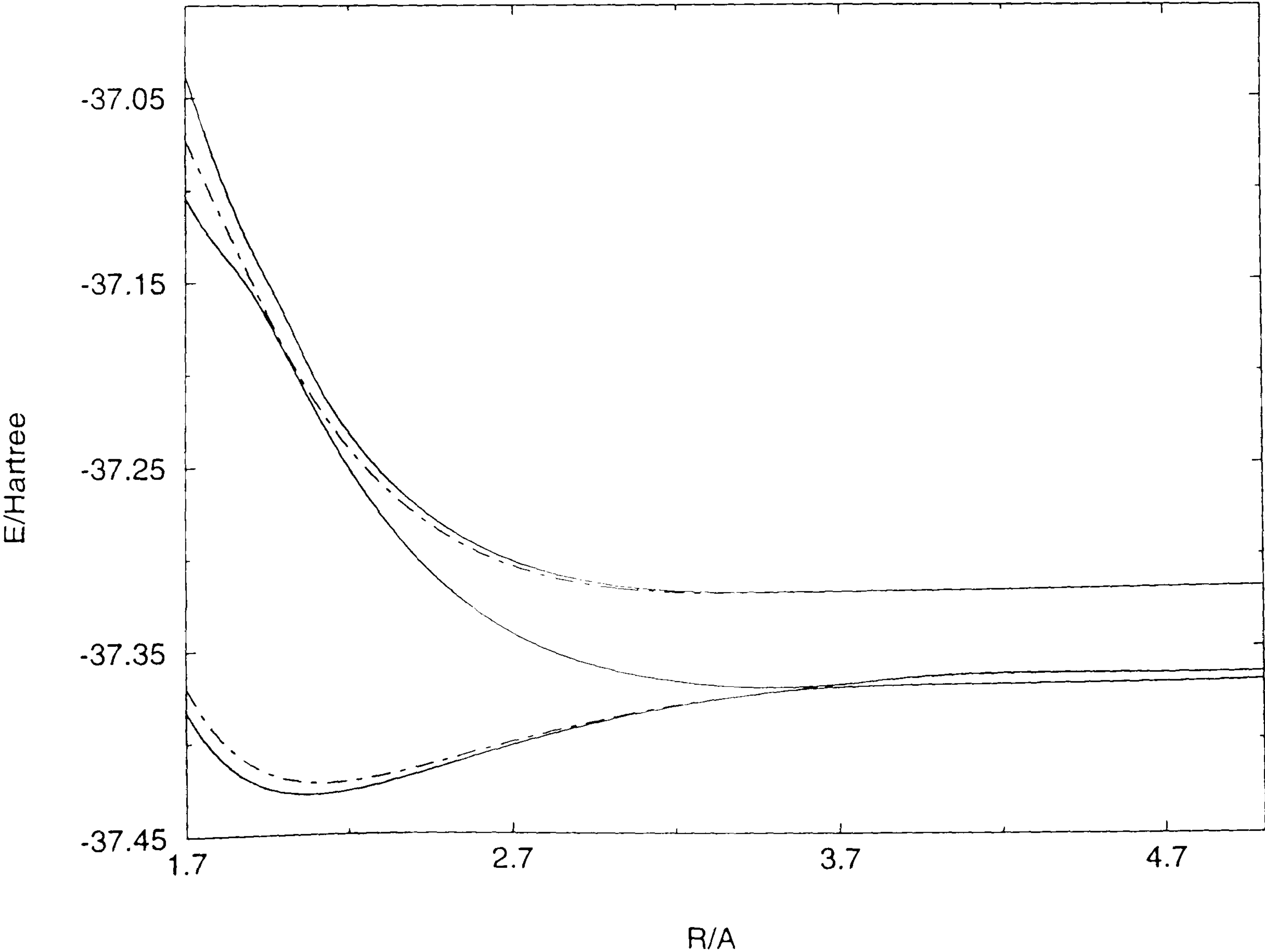
B.4.12 The CI results for the $^4\Sigma^-$ states of BBr^+ with the VQZ basis sets

Table B.4.12 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.7	-37.382629	-37.369484	-37.103334	-37.071953	-37.037028
1.8	-37.407823	-37.396835	-37.130818	-37.110394	-37.088495
1.9	-37.421501	-37.412392	-37.154330	-37.147898	-37.130998
2.0	-37.427542	-37.420049	-37.186124	-37.184374	-37.165839
2.1	-37.428794	-37.422628	-37.219676	-37.214902	-37.202848
2.2	-37.426970	-37.421913	-37.250379	-37.239721	-37.231292
2.3	-37.423285	-37.419142	-37.276900	-37.259638	-37.253251
2.4	-37.418555	-37.415161	-37.298880	-37.275444	-37.270367
2.5	-37.413321	-37.410536	-37.316649	-37.287842	-37.283714
2.6	-37.407911	-37.405615	-37.330839	-37.297449	-37.294053
2.7	-37.402658	-37.400765	-37.341924	-37.304752	-37.301953
2.8	-37.397667	-37.396101	-37.350500	-37.310225	-37.307915
2.9	-37.393041	-37.391742	-37.357052	-37.314229	-37.312321
3.0	-37.388841	-37.387764	-37.361990	-37.317054	-37.315481
3.1	-37.385106	-37.384218	-37.365658	-37.318967	-37.317665
3.2	-37.381832	-37.381113	-37.368317	-37.320136	-37.319066
3.5	-37.374547	-37.374534	-37.371975	-37.320785	-37.320145
4.0	-37.370750	-37.366266	-37.365877	-37.320052	-37.319770
4.5	-37.369717	-37.364574	-37.364383	-37.318790	-37.318651
5.0	-37.368456	-37.364035	-37.363930	-37.317699	-37.317619

E/Hartree

Figure B.4.12 Calculated potential energy curves



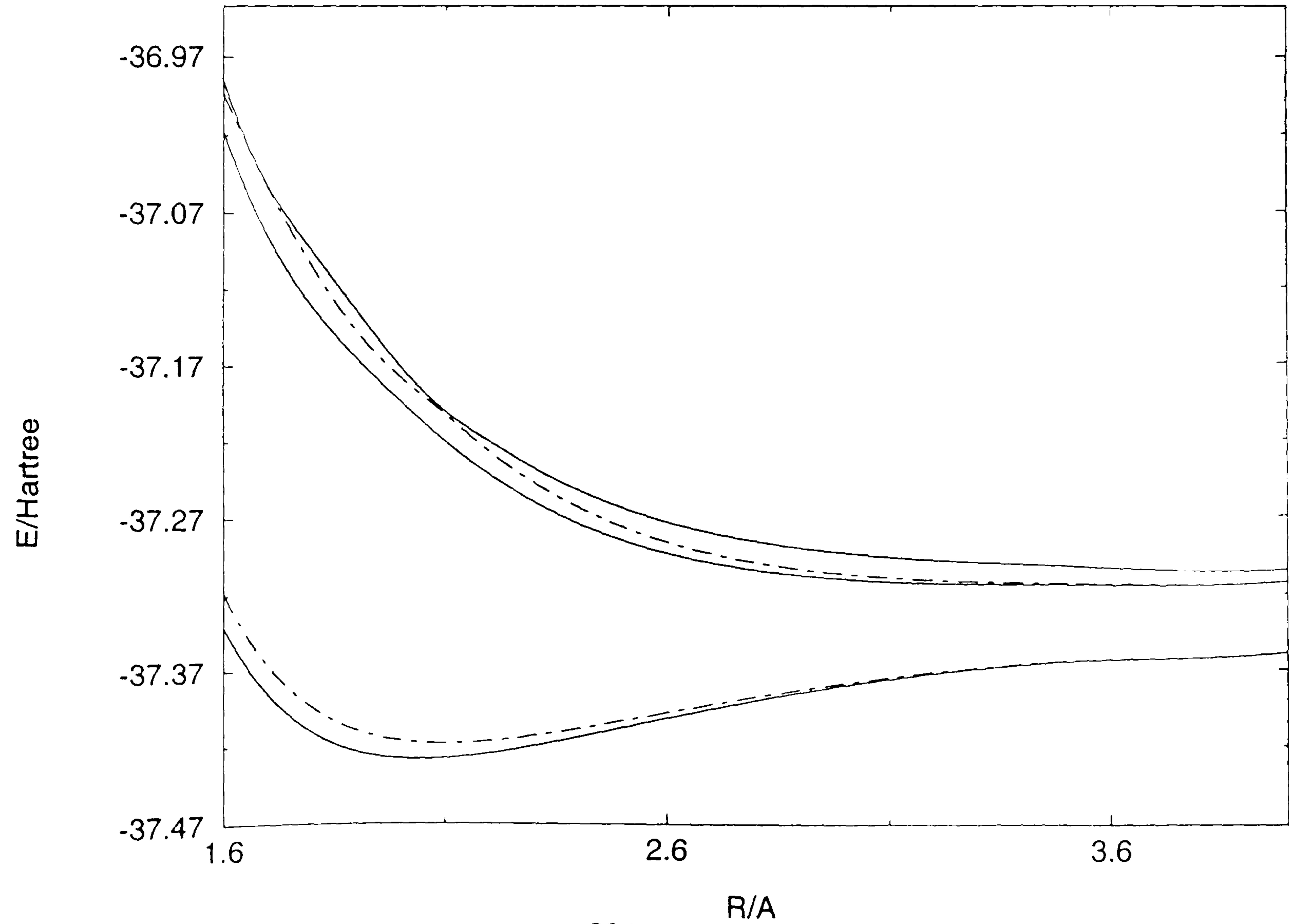
B.4.13 The CI results for the $^4\Sigma^+$ states of BBr^+ with the VDZ basis sets

Table B.4.13 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.6	-37.340934	-37.318927	-37.018080	-36.993927	-36.985447
1.7	-37.385134	-37.366056	-37.084670	-37.053101	-37.051663
1.8	-37.410407	-37.394061	-37.130905	-37.104414	-37.094335
1.9	-37.423283	-37.409406	-37.164710	-37.146880	-37.133317
2.0	-37.428109	-37.416420	-37.193380	-37.177720	-37.170949
2.1	-37.427915	-37.418146	-37.219803	-37.202054	-37.200045
2.2	-37.424641	-37.416531	-37.241924	-37.227197	-37.220140
2.3	-37.419607	-37.412915	-37.259662	-37.247321	-37.237797
2.4	-37.413683	-37.408192	-37.273635	-37.263304	-37.252220
2.5	-37.407439	-37.402952	-37.284520	-37.275907	-37.263716
2.6	-37.401232	-37.397578	-37.292912	-37.285765	-37.272798
2.7	-37.395290	-37.392321	-37.299317	-37.293415	-37.279950
2.8	-37.389750	-37.387339	-37.304141	-37.299289	-37.285570
2.9	-37.384692	-37.382732	-37.307714	-37.303739	-37.289983
3.0	-37.380157	-37.378558	-37.310296	-37.307049	-37.293442
3.1	-37.376157	-37.374849	-37.312097	-37.309450	-37.296155
3.2	-37.372687	-37.371610	-37.313281	-37.311129	-37.298280
3.5	-37.365131	-37.364503	-37.314378	-37.313228	-37.302277
4.0	-37.359009	-37.358713	-37.312371	-37.311942	-37.304506

E/Hartree

Figure B.4.13 Calculated potential energy curves



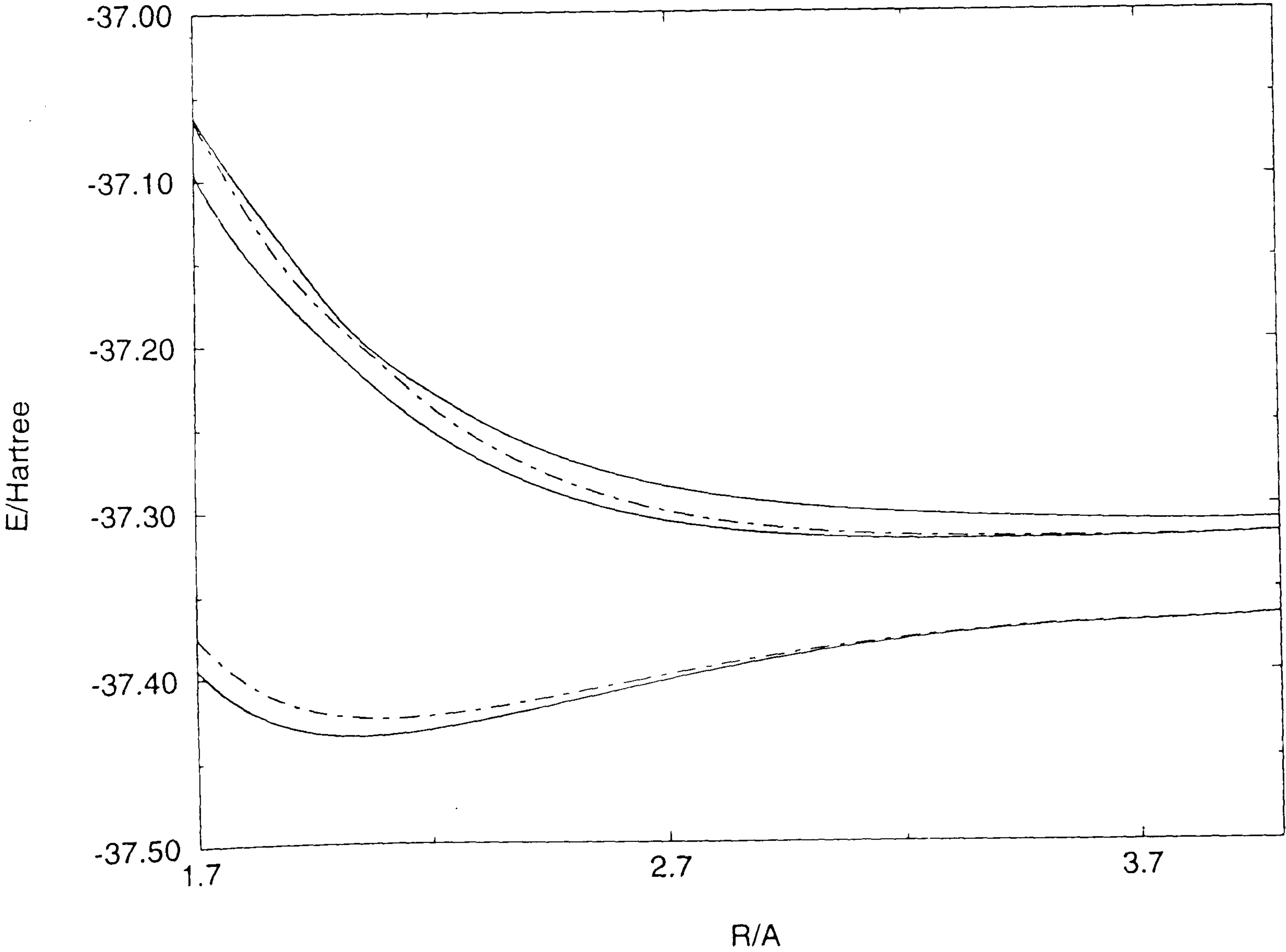
B.4.14 The CI results for the $^4\Sigma^+$ states of BBr^+ with the VTZ basis sets

Table B.4.14 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.7	-37.393980	-37.374939	-37.095571	-37.063827	-37.061205
1.8	-37.417906	-37.401501	-37.140886	-37.112593	-37.104300
1.9	-37.430273	-37.416288	-37.174232	-37.154784	-37.142695
2.0	-37.435043	-37.423231	-37.202522	-37.185633	-37.180209
2.1	-37.435015	-37.425129	-37.228801	-37.211327	-37.207696
2.2	-37.431964	-37.423756	-37.250963	-37.236513	-37.227531
2.3	-37.427123	-37.420353	-37.268737	-37.256627	-37.245208
2.4	-37.421321	-37.415771	-37.282671	-37.272514	-37.259616
2.5	-37.415118	-37.410588	-37.293422	-37.284927	-37.270975
2.6	-37.408886	-37.405202	-37.301592	-37.294515	-37.279840
2.7	-37.402877	-37.399887	-37.307701	-37.301829	-37.286729
2.8	-37.397248	-37.394824	-37.312176	-37.307324	-37.292065
2.9	-37.392099	-37.390131	-37.315368	-37.311373	-37.296194
3.0	-37.387481	-37.385877	-37.317556	-37.314279	-37.299384
3.1	-37.383409	-37.382097	-37.318966	-37.316285	-37.301847
3.2	-37.379875	-37.378795	-37.319779	-37.317595	-37.303748
3.5	-37.372156	-37.371526	-37.319960	-37.318793	-37.307234
4.0	-37.365808	-37.365511	-37.317156	-37.316725	-37.309030

E/Hartree

Figure B.4.14. Calculated potential energy curves



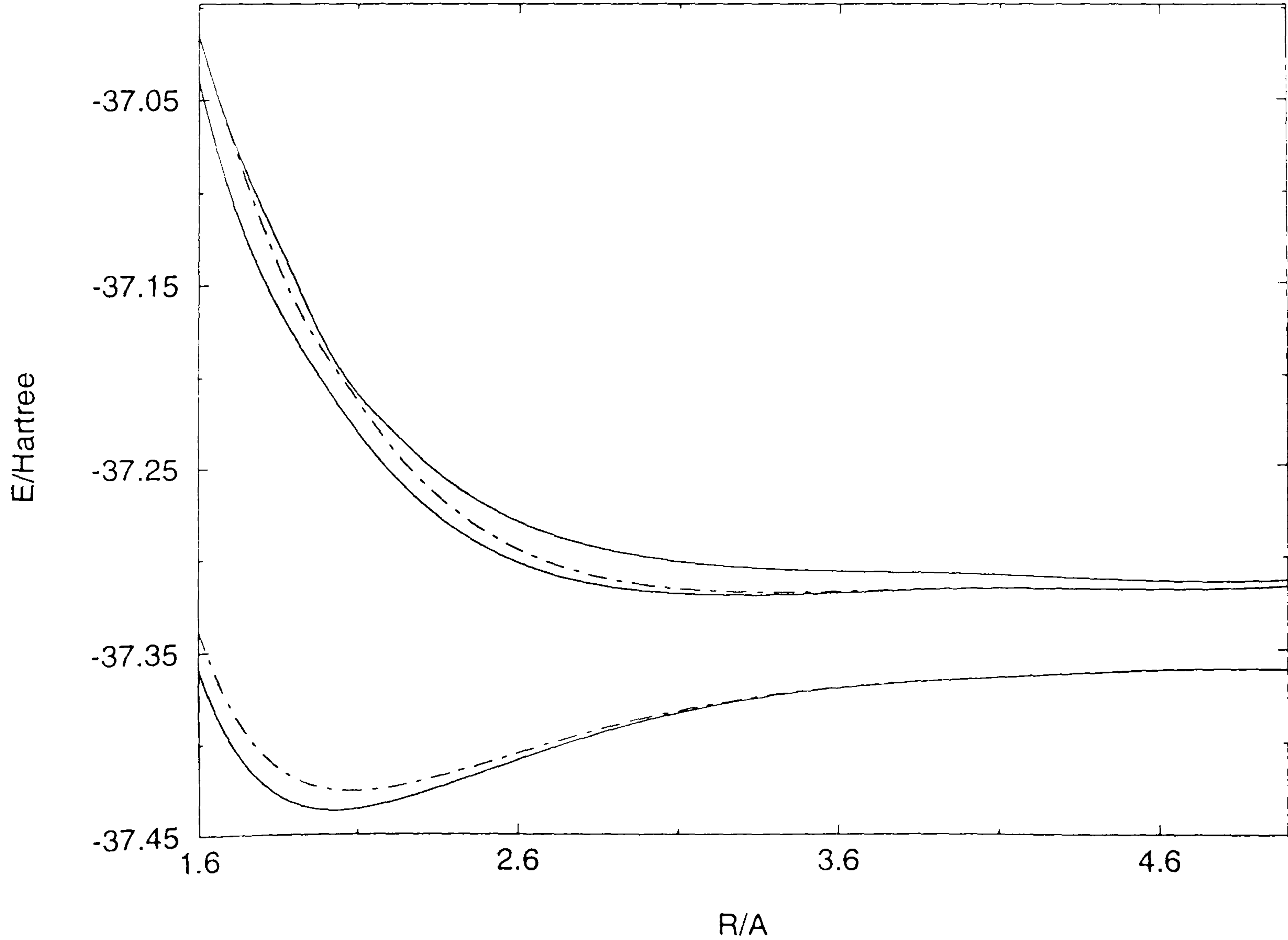
B.4.15 The CI results for the $^4\Sigma^+$ states of BBr^+ with the VQZ basis sets

Table B.4.15 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4	ROOT5
1.6	-37.361842	-37.339914	-37.041113	-37.016570	-37.016026
1.7	-37.401558	-37.382479	-37.103396	-37.071652	-37.069937
1.8	-37.424106	-37.407703	-37.147233	-37.119532	-37.110590
1.9	-37.435344	-37.421380	-37.179430	-37.160239	-37.147890
2.0	-37.439223	-37.427435	-37.206857	-37.189922	-37.184563
2.1	-37.438526	-37.428658	-37.232463	-37.215029	-37.211106
2.2	-37.435010	-37.426810	-37.254169	-37.239779	-37.230315
2.3	-37.429878	-37.423110	-37.271681	-37.259631	-37.247670
2.4	-37.423926	-37.418371	-37.285489	-37.275378	-37.261944
2.5	-37.417671	-37.413134	-37.296195	-37.287730	-37.273264
2.6	-37.411449	-37.407755	-37.304360	-37.297295	-37.282135
2.7	-37.405480	-37.402479	-37.310475	-37.304601	-37.289046
2.8	-37.399901	-37.397463	-37.314947	-37.310083	-37.294405
2.9	-37.394796	-37.392815	-37.318119	-37.314106	-37.298549
3.0	-37.390211	-37.388594	-37.320269	-37.316970	-37.301741
3.2	-37.382627	-37.381534	-37.322369	-37.320163	-37.306068
3.3	-37.379590	-37.378682	-37.322654	-37.320856	-37.307503
3.5	-37.374835	-37.374194	-37.322315	-37.321133	-37.309416
4.0	-37.368241	-37.367938	-37.319160	-37.318725	-37.310927
4.5	-37.364174	-37.364018	-37.319703	-37.319517	-37.314618
5.0	-37.363567	-37.363476	-37.318301	-37.318202	-37.315029

E/Hartree

Figure B.4.15 Calculated potential energy curves



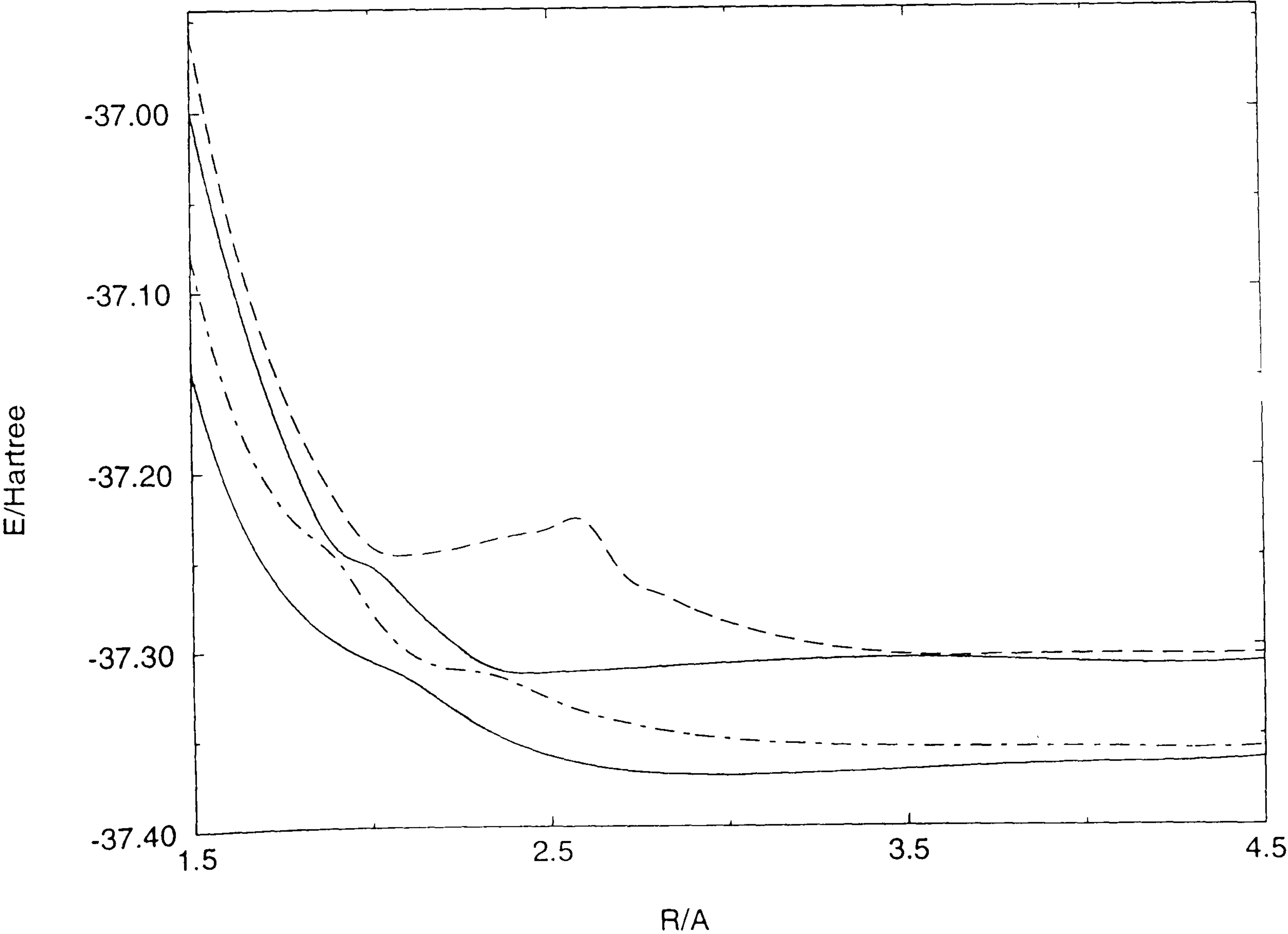
B.4.16 The CI results for the $^4\Pi$ states of BBr^+ with the VDZ basis sets

Table B.4.16 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4
1.5	-37.142354	-37.078185	-36.998494	-36.955060
1.6	-37.209302	-37.155671	-37.082010	-37.052976
1.7	-37.252135	-37.203095	-37.148972	-37.123696
1.8	-37.279240	-37.230694	-37.203243	-37.176148
1.9	-37.296287	-37.249031	-37.242699	-37.215754
2.0	-37.307363	-37.280253	-37.254117	-37.242792
2.1	-37.317131	-37.302302	-37.273994	-37.247589
2.2	-37.331090	-37.311024	-37.292824	-37.245177
2.3	-37.344231	-37.313676	-37.307956	-37.241009
2.4	-37.354148	-37.320156	-37.314157	-37.236548
2.5	-37.361182	-37.329589	-37.313881	-37.232590
2.6	-37.365959	-37.336970	-37.313057	-37.229778
2.7	-37.369197	-37.342301	-37.312047	-37.258625
2.8	-37.370959	-37.346472	-37.311044	-37.270200
2.9	-37.371813	-37.349586	-37.310054	-37.279567
3.0	-37.372040	-37.351884	-37.309128	-37.287042
3.1	-37.371848	-37.353558	-37.308299	-37.292924
3.2	-37.371391	-37.354760	-37.307588	-37.297482
3.5	-37.369324	-37.356577	-37.306683	-37.304935
4.0	-37.365771	-37.357094	-37.309576	-37.304835
4.5	-37.363022	-37.356841	-37.309392	-37.304786

E/Hartree

Figure B.4.16 Calculated potential energy curves



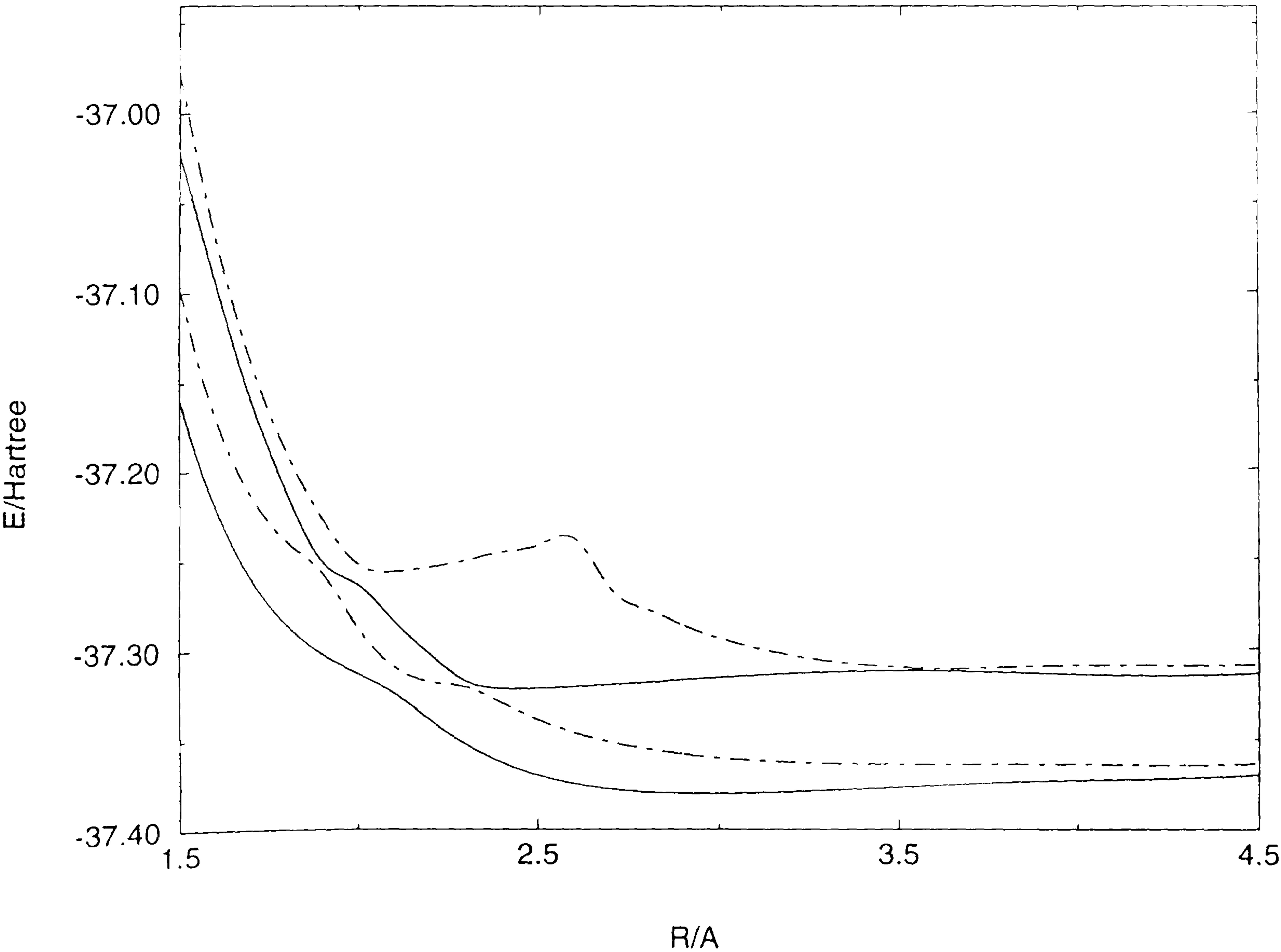
B.4.17 The CI results for the $^4\Pi$ states of BBr^+ with the VTZ basis sets

Table B.4.17 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4
1.5	-37.158104	-37.095880	-37.021977	-36.975633
1.6	-37.220122	-37.168454	-37.093578	-37.068724
1.7	-37.260121	-37.213160	-37.158020	-37.136931
1.8	-37.285820	-37.239519	-37.211233	-37.188023
1.9	-37.302362	-37.257168	-37.250798	-37.226773
2.0	-37.313550	-37.288060	-37.263763	-37.252224
2.1	-37.324265	-37.309715	-37.284318	-37.256251
2.2	-37.339279	-37.318014	-37.302932	-37.254006
2.3	-37.352734	-37.320925	-37.317736	-37.249967
2.4	-37.362729	-37.329757	-37.321510	-37.245536
2.5	-37.369724	-37.338928	-37.321289	-37.241510
2.6	-37.374391	-37.346027	-37.320396	-37.238423
2.7	-37.377478	-37.351082	-37.319172	-37.266269
2.8	-37.379074	-37.354973	-37.317917	-37.277491
2.9	-37.379765	-37.357825	-37.316635	-37.286499
3.0	-37.379840	-37.359888	-37.315401	-37.293625
3.1	-37.379513	-37.361352	-37.314273	-37.299179
3.2	-37.378939	-37.362370	-37.313286	-37.303438
3.5	-37.376595	-37.363755	-37.311864	-37.310062
4.0	-37.372681	-37.363851	-37.314197	-37.309362
4.5	-37.369660	-37.363400	-37.313775	-37.309144

E/Hartree

Figure B.4.17 Calculated potential energy curves



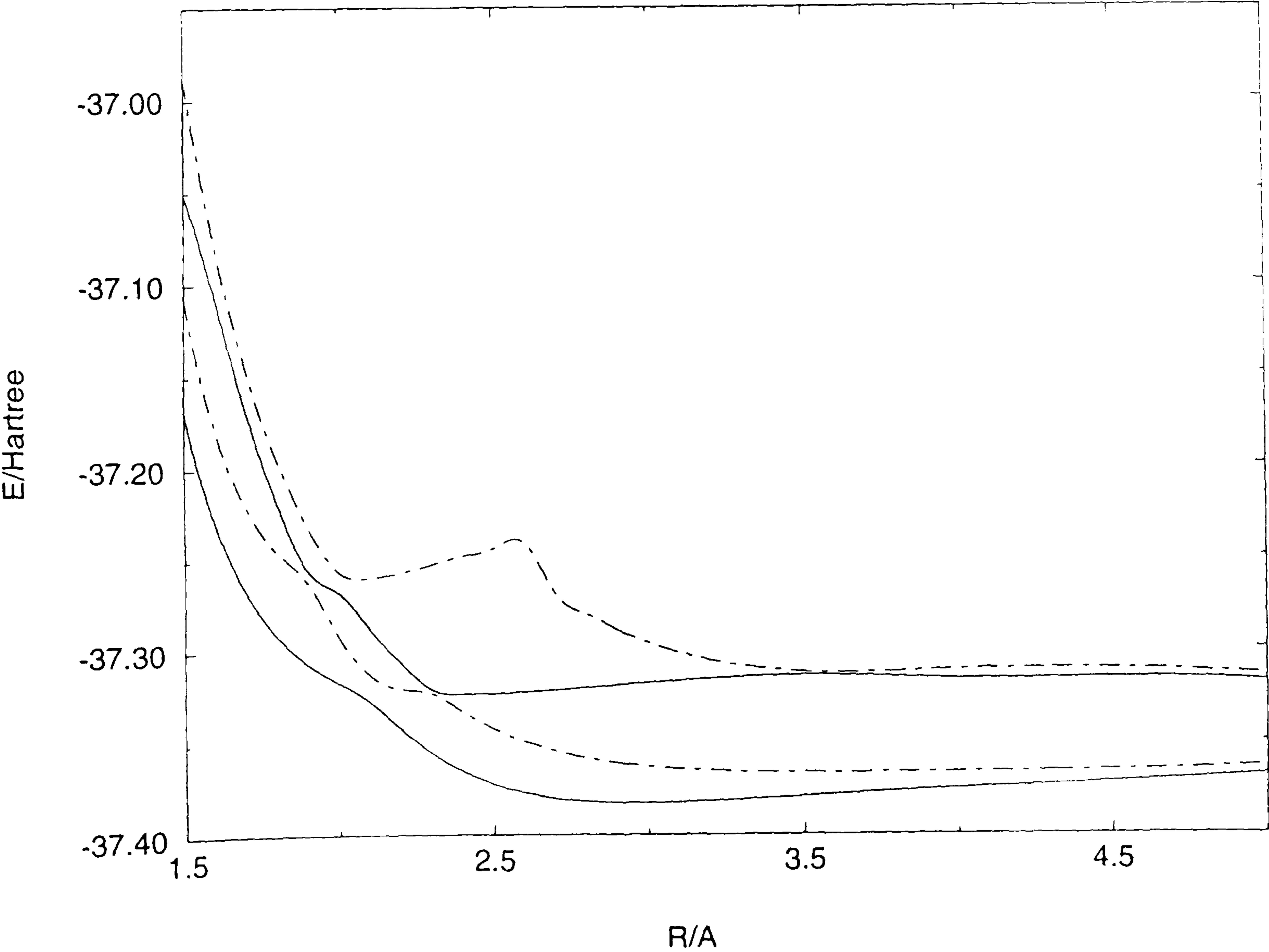
B.4.18 The CI results for the $^4\Pi$ states of BBr^+ with the VQZ basis sets

Table B.4.18 Theoretical energy values

R/Å	ROOT1	ROOT2	ROOT3	ROOT4
1.5	-37.168692	-37.106592	-37.049839	-36.987031
1.6	-37.229243	-37.177598	-37.106263	-37.078444
1.7	-37.267708	-37.220700	-37.167417	-37.144870
1.8	-37.292036	-37.245709	-37.218673	-37.194559
1.9	-37.307395	-37.262707	-37.256151	-37.232229
2.0	-37.317620	-37.292618	-37.268188	-37.256617
2.1	-37.327739	-37.313209	-37.288399	-37.259756
2.2	-37.342414	-37.320727	-37.306662	-37.257034
2.3	-37.355625	-37.323330	-37.321128	-37.252722
2.4	-37.365523	-37.333130	-37.323591	-37.248164
2.5	-37.372517	-37.342233	-37.323301	-37.244107
2.6	-37.377233	-37.349294	-37.322437	-37.241025
2.7	-37.380387	-37.354321	-37.321290	-37.268866
2.8	-37.382040	-37.358172	-37.320131	-37.280101
2.9	-37.382768	-37.360973	-37.318934	-37.289104
3.0	-37.382865	-37.362974	-37.317762	-37.296211
3.1	-37.382542	-37.364367	-37.316663	-37.301723
3.2	-37.381957	-37.365307	-37.315676	-37.305924
3.5	-37.379526	-37.366454	-37.314136	-37.312315
4.0	-37.375365	-37.366214	-37.316116	-37.311264
4.5	-37.372067	-37.365556	-37.315472	-37.310818
5.0	-37.367801	-37.363232	-37.317881	-37.314140

E/Hartree

Figure B.4.18 Calculated potential energy curves



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